Honeywell
THE POWER OF CONNECTED

July 21, 2017

Dr. Souad A. Benromdhane
Environmental Engineer/Physical Scientist
Risk and Benefits Group
U.S. Environmental Protection Agency
HEID, OAQPS, Mail drop: (C539-07)
Research Triangle Park, NC 27711

Dear Dr. Benromdhane,

Honeywell International, Inc. (Honeywell or Company) requests the U.S. Environmental Protection Agency (EPA or Agency) to exempt the chemical (Z)-1-chloro-3, 3, 3-trifluoro-1-propene, HCFO-1233zd(Z), (cis-1233zd (Z)) [CAS RN 99728-16-2], from the Agency's definition of the term, volatile organic compound (VOC). This exemption would allow cis-1233zd(Z) to be used in the U.S. without regulation as a potential precursor to tropospheric ozone under the requirements in 40 CFR 51.100(s). cis-1233zd(Z) has very low potential to generate ozone in the troposphere. Its maximum incremental reactivity (MIR) value is 0.08, which is three times less than that for ethane on a mass basis (Carter 2017).

Below is a summary of data from the peer-reviewed scientific literature on the atmospheric reactivity of cis-1233zd(Z) and the propensity of this molecule not to contribute to tropospheric ozone formation.

Basis for (Z)-1-chloro-3, 3, 3-trifluoro-1-propene HCFO-1233zd(Z), (cis-1233zd (Z)) VOC exemption

1. **Atmospheric Chemistry of cis-1233zd(Z) (Attachment 1)**

   The atmospheric chemistry of cis-1233zd(Z) was examined in experiments by Andersen *et. al [1].* (FTIR) *Fourier* transform infrared smog chamber techniques were used to measure the rate coefficients of Cl atoms, OH radicals and O_3 with cis-1233zd(Z). The atmospheric lifetime of cis-1233zd(Z) was determined by reaction with OH radicals. It was estimated to be 14 days.

   The infrared spectrum of cis-1233zd(Z) was recorded and the integrated absorption over the range 600–2000 cm^{-1} was measured to be $(1.48 \pm 0.07) \times 10^{-16}$cm $molecule^{-1}$. Accounting for non-uniform horizontal and vertical mixing leads to a GWP 100 value of < 1. Utilizing previous relative rate studies of OH and trans-CF_3CH=CHCl to adjust for unwanted Cl atom chemistry gives k (OH + trans-CF_3CH= CHCl) =$(3.61 \pm 0.37) \times 10^{-13}$ cm^3 $molecule^{-1}s^{-1}$.

2. **Ozone Impact of cis-1233zd(Z): Maximum Incremental Reactivity (MIR) (Attachment 2)**

   The maximum incremental reactivity (MIR) of cis-1233zd(Z) was estimated in experiments by Carter 2017. Previous experimental and modeling studies with trans-1-chloro-3,3,3-trifluoropropene (CF3CH= CHCl), has shown average ratio of mass-based incremental reactivities relative to ethane for all the box model scenarios

of 0.19±0.03 and the MIR ratio was 0.16±0.02. It was concluded that if ethane is used as the standard to define "negligible" ozone impact for the purpose of determining VOC exemptions for ozone precursors, then trans 1-chloro-3,3,3-trifluoropropene will meet this standard. Trans 1-chloro-3,3,3-trifluoropropene was also found to have no significant effect on particle formation in the incremental reactivity chamber experiments. This means that if all other aspects of the mechanisms are similar, as is expected to be the case if the only difference is the cis vs. trans configuration, then the ratios in the reactivities would be approximately proportional to the ratios in their OH rate constants. Since the cis isomer has an OH rate constant that is 1.9 times higher used to calculate the reactivities of the trans isomer, then the reactivities for the cis isomer should be approximately than those for the trans isomer, multiplied by 1.9. That means we estimate that the ozone impact of the cis isomer relative to ethane for all the box model scenarios to be 0.36±0.06 and the MIR ratio to be 0.30±0.04. Although the ozone impact for the cis isomer is estimated to be about twice that for the trans isomer, it is still about three times less than that for ethane on a mass basis.

It is therefore concluded that if ethane is used as the standard to define "negligible" ozone impact for the purpose of determining VOC exemptions for ozone precursors, then cis 1-chloro-3,3,3-trifluoropropene will meet this standard.

3. **<u>Ozone Impact of cis-1233zd(Z): Photochemical Ozone Creation Potential (Attachment 3)</u>**
Reactivity-based VOC regulations require means to quantify ozone impacts for VOCs. The Photochemical Ozone Creation Potential (POCP) is a scale for assessing the ozone production associated with releases of a given VOC. POCP uses a photochemical air quality model to calculate the total additional ozone formed over about five days after a given release of a volatile organic compound. Ethane which has a POCP of 100 is oxidized sufficiently slowly that is does not contribute to any appreciable degree to local air quality issues and are generally exempt from air quality regulations. The POCP of cis-1233zd is 6.4 which is far below that of ethane.

Cis-1233zd has an atmospheric lifetime which is approximately half that of trans-1233zd (Andersen et al., 2014) and hence the ODP for cis-1233zd will be even lower than that for trans-1233zd. The ODP of cis-1233zd would be < 0.00034. Patten and Wuebbles (2010) concluded that at the concentrations likely to be emitted trans-1233zd is unlikely to affect stratospheric ozone. Haloolefins have ODPs which are zero, or near zero, and will not impact stratospheric ozone.

4. **Toxicological and Ecotoxicology profile of Cis-1-chloro-3,3,3-trifluoropropene**

Toxicology: Acute inhalation toxicity of cis-1-chloro-3,3,3-trifluoropropene [1233zd(Z)] has been evaluated in rats with a 4h LC50 between 36,021 and 53,352 ppm. Cardiac sensitization threshold, evaluated in beagle dogs through inhalation route of exposure, is 5000 ppm and No Observed Effect Level (NOEL) is 2500 ppm. Longest duration repeated-dose exposure study available for this molecule is a 13-week exposure study through inhalation route of exposure in rats. In this study, there were no adverse effects observed at 5000 ppm, the highest concentration tested. Genotoxicity profile of 1233zd(Z) is characterized through several in vitro and in vivo assays. 1233zd(Z) is not genotoxic.

Ecotoxicology: 1233zd(Z) has been tested for its ecotoxicological properties in algae, daphnia and fish. The 72h EC50 in algae is >97.5 mg/L and the No Observed Effect Concentration (NOEC) is 41.0 mg/L. In daphnia, the 48h EC50 is 27.6 mg/L and NOEC is 21.4 mg/L. Toxicity test conducted in rainbow trout demonstrated a 96h LC50 of 46.8 mg/L and NOEC of 4.22 mg/L. A study is available to evaluate the biodegradability of 1233zd(Z). In this study, 1233zd(Z) was not biodegraded by the microorganisms under the test conditions. Overall, 1233zd(Z) has relatively low toxicity to aquatic organisms.

Use of cis-1233zd(Z)

Cis-1233zd(Z) is used mainly as a cleaning agent in precision cleaning of components, such as metal and electronics precision cleaning applications and is expected to be a 1 to 1 replacement of ODS substances. Cis-1233zd(Z) can be blended with other chemicals is used to remove either highly fluorinated oils, hydrocarbon-based oils, grease, fluxes and non-volatile residues from industrial surfaces and parts. For aerosol applications, Cis-1233zd(Z) is expected to replace ODS substances at a ratio of two in non-flammable energized electrical contact cleaners for general cleaning applications and flux removal. In carrier fluid applications such as adhesives and coatings, Cis-1233zd(Z) is also expected to replace ODS substances in a ratio of 1 to 1. These applications rely on Cis-1233zd(Z) characteristics such as solvency power, non-flammable, low environmental impact, dielectric properties, surface tension, vapor pressure, viscosity and low toxicity profile.

Justification for expedited petition ruling

The development of measures to reduce ozone concentrations is leading to the phase out of products with Ozone Depletion Potentials (ODP) and high Global Warming Potentials (GWP). Cis-1233zd(Z) is an HFO with low (<1) GWP and Zero ODP. Cis-1233zd(Z) can be used to replace high GWP and ODP industrial solvents, foam blowing agents and refrigerants. If the VOC exemption under the Federal Clean Air Act is granted, cis-1233zd(Z) will be an effective substitute in the development of environmentally sustainable solutions that reduce ozone formation. Cis-1233zd(Z) is relatively low to aquatic organisms and is not classified as a hazardous substance or mixture according to the Occupational Safety and Health Administration (OSHA) Hazard Communications Standard 2012. The cis-1233zd(Z) VOC exemption will help the precision cleaning, and aerosol industries meet their sustainability goals since the use of cis-1233zd(Z) as a low GWP and Zero

Honeywell
THE POWER OF CONNECTED

ODP can significantly reduce their greenhouse gas emissions. The Premanufacture Notice (PMN # 17-0267) and a SNAP addendum application under the Significant New Alternatives Policy program have been submitted and are under review.

Conclusion

Based on the atmospheric chemistry and the ozone impact presented in this petition, Honeywell requests that the US EPA grant cis-1233zd(Z) a VOC exemption.

Please contact the following people if you have any questions about this request or need further clarification.

Sincerely,

Nicole Sandomenico
Lead Specialist, Product Stewardship
Telephone: 973-455-3102
Email: nicole.sandomenico@honeywell.com

Dr. Sandeep Mukhi
Principle Specialist, Toxicology
Telephone: 973-455-5186
Email: sandeep.mukhi@honeywell.com

Honeywell
THE POWER OF CONNECTED

References

1 Andersen, L.L., et al., Atmospheric chemistry of cis-$CF_3CH=CHCl$ (HCFO-1233zd(Z)): Kinetics of the gas-phase reactions with Cl atoms, OH radicals, and O_3. Chemical Physics Letters 639, 2015: p. 289-293.

2 Carter, W.P.L., Estimation of Ground Level Atmospheric Ozone Impacts of Cis 1-Chloro-3,3,3-Trifluoropropene, Final Report to Honeywell International Inc., March 2017: p. 1-4.

3 Wallington, T.J., et al., Atmospheric chemistry of short-chain haloolefins: Photochemical ozone creation potentials (POCPs), global warming potentials (GWPs), and ozone depletion potentials (ODPs), Chemosphere 129, 2015: p. 135-141.

4 cis-1-Chloro-3,3,3-Trifluoropropene Safety Data Sheet (SDS)

Chemical Physics Letters 639 (2015) 289–293

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Atmospheric chemistry of *cis*-$CF_3CH{=}CHCl$ (HCFO-1233zd(Z)): Kinetics of the gas-phase reactions with Cl atoms, OH radicals, and O_3

Lene Løffler Andersen [a,*], Freja From Østerstrøm [a], Mads P. Sulbaek Andersen [a,b], Ole John Nielsen [a], Timothy J. Wallington [c]

[a] Copenhagen Center for Atmospheric Research, Department of Chemistry, University of Copenhagen, Universitetsparken 5, 2100 Copenhagen, Denmark
[b] Department of Chemistry and Biochemistry, California State University Northridge, 18111 Nordhoff St., Northridge, CA 91330-8262, USA
[c] System Analytics and Environmental Sciences Department, Ford Motor Company, Mail Drop RIC-2122, Dearborn, MI 48121-2053, USA

ARTICLE INFO

Article history:
Received 17 June 2015
In final form 3 September 2015
Available online 25 September 2015

ABSTRACT

FTIR smog chamber techniques were used to measure the rate coefficients $k(Cl + cis\text{-}CF_3CH{=}CHCl) = (6.26 \pm 0.84) \times 10^{-11}$, $k(OH + cis\text{-}CF_3CH{=}CHCl) = (8.45 \pm 1.52) \times 10^{-13}$, and $k(O_3 + cis\text{-}CF_3CH{=}CHCl) = (1.53 \pm 0.12) \times 10^{-21}$ cm^3 molecule^{-1} s^{-1}. The atmospheric lifetime of *cis*-$CF_3CH{=}CHCl$ is determined by reaction with OH radicals and is estimated to be 14 days. The infrared spectrum of *cis*-$CF_3CH{=}CHCl$ was recorded and the integrated absorption over the range 600–2000 cm^{-1} was measured to be $(1.48 \pm 0.07) \times 10^{-16}$ cm molecule^{-1}. Accounting for non-uniform horizontal and vertical mixing leads to a GWP_{100} value of essentially zero. Correction to account for unwanted Cl atom chemistry in our previous relative rate study of the kinetics of the reaction of OH with *trans*-$CF_3CH{=}CHCl$ gives $k(OH + trans\text{-}CF_3CH{=}CHCl) = (3.61 \pm 0.37) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

1. Introduction

Recognition of the environmental consequences of the release of chlorofluorocarbons (CFCs) and halons into the atmosphere [1,2] has led to an international effort to replace these compounds with environmentally acceptable alternatives. While protection of the ozone layer has been the focus of these efforts, concerns related to global climate change are becoming an increasingly important consideration in the choice of alternative compounds.

Saturated hydrofluorocarbons (HFCs), such as CF_3CFH_2 (HFC-134a), have become widely used CFC replacements. HFCs do not contain chlorine and therefore do not contribute to chlorine-based catalytic destruction of stratospheric ozone [3]. Haloolefins are a new generation of CFC replacements which are being developed. Haloolefins have a greater reactivity than HFCs toward OH radicals and hence have shorter atmospheric lifetimes and smaller global warming potentials. *cis*-1-chloro-3,3,3-trifluoropropene (*cis*-$CF_3CH{=}CHCl$, HCFO-1233zd(Z)) is a haloolefin which has been developed for use in degreasing of mechanical parts and in dry cleaning. *cis*-$CF_3CH{=}CHCl$ contains a chlorine atom that potentially can participate in the destruction of the ozone layer. However, if the atmospheric lifetime of *cis*-$CF_3CH{=}CHCl$ is sufficiently low, the compound will not reach the stratosphere, and thus not participate in the catalytic destruction of the ozone layer. Prior to large-scale industrial use an assessment of the atmospheric chemistry and environmental impact of *cis*-$CF_3CH{=}CHCl$ is needed. To fulfill this need we have conducted an experimental investigation of the atmospheric chemistry of *cis*-$CF_3CH{=}CHCl$. Experiments were conducted in the smog chamber at Ford Motor Company (Ford), Michigan, USA, and in the photoreactor at the Copenhagen Center for Atmospheric Research (CCAR) at University of Copenhagen, Denmark. Fourier transform infrared (FTIR) smog chamber techniques were used to determine the kinetics of the gas-phase reactions of Cl atoms, OH radicals, and O_3 with *cis*-$CF_3CH{=}CHCl$. The IR spectrum of *cis*-$CF_3CH{=}CHCl$ was measured and the global warming potential (GWP) of *cis*-$CF_3CH{=}CHCl$ was calculated.

2. Experimental method

The experimental procedures are described in detail elsewhere [4] and only a brief summary is given here. Chlorine atoms were generated by photolysis of molecular chlorine:

$$Cl_2 + h\nu \rightarrow 2Cl \quad (1)$$

* Corresponding author.
E-mail address: lene.lla@hotmail.com (L.L. Andersen).

http://dx.doi.org/10.1016/j.cplett.2015.09.008
0009-2614/

Hydroxyl radicals (OH) were generated by UV irradiation of methyl nitrite (CH_3ONO) in air in the presence of nitric oxide:

$$CH_3ONO + h\nu \rightarrow CH_3O + NO \quad (2)$$

$$CH_3O + O_2 \rightarrow HO_2 + HCHO \quad (3)$$

$$HO_2 + NO \rightarrow OH + NO_2 \quad (4)$$

The concentrations of reactants and products were monitored using in situ FTIR spectroscopy. Analysis of the spectra was carried out by a process of spectral stripping in which scaled reference spectra were subtracted from the sample spectrum. Reference spectra were acquired by expanding known volumes of reference compounds into the reaction chambers.

The relative rate method is a well-established technique for measuring the rate coefficients of chlorine atoms or OH radicals with organic compounds. Kinetic data were derived by monitoring the loss of *cis*-$CF_3CH{=}CHCl$ relative to one or more reference compounds. The decays of the reactant and reference are then plotted using the expression:

$$\mathrm{Ln}\left(\frac{[cis\text{-}CF_3CH{=}CHCl]_{t_0}}{[cis\text{-}CF_3CH{=}CHCl]_t}\right) = \frac{k_{\mathrm{Reactant}}}{k_{\mathrm{Reference}}}\mathrm{Ln}\left(\frac{[\mathrm{Reference}]_{t_0}}{[\mathrm{Reference}]_t}\right) \quad (I)$$

where $[cis\text{-}CF_3CH{=}CHCl]_{t_0}$, $[cis\text{-}CF_3CH{=}CHCl]_t$, $[\mathrm{Reference}]_{t_0}$ and $[\mathrm{Reference}]_t$ are the concentrations of *cis*-$CF_3CH{=}CHCl$ and the reference compound at times t_0 and t. The slope is then the ratio of the rate coefficient for reaction of either Cl atoms or OH radicals toward *cis*-$CF_3CH{=}CHCl$ and the corresponding reaction for the reference compound.

The kinetics of the O_3 reaction were studied using an absolute rate method, in which the pseudo first order loss of reactant was measured in the presence of excess O_3. A linear plot of the pseudo-first order rate coefficients versus the initial O_3 concentration gives a slope of k_5.

$$O_3 + cis\text{-}CF_3CH{=}CHCl \rightarrow \text{Products} \quad (5)$$

In smog chamber experiments unwanted loss of reactants, reference compounds, and products via photolysis and heterogeneous reactions need to be considered. To test for the presence of heterogeneous reactions, mixtures obtained after UV irradiation were allowed to stand in the dark in the chamber for 30 min. There was no observable (<2%) loss of reactants or products, suggesting that heterogeneous reactions are not a significant complication in the present experiments.

Potential systematic uncertainties inherent in the analysis of the IR spectra are typically ±1% of the initial reactant concentration. Unless otherwise stated, we choose to cite final values with error limits, which include two standard deviations from the least squares regression and 5% uncertainty in the reactant calibrations. *cis*-$CF_3CH{=}CHCl$ was supplied by Honeywell International Inc. with a purity of >99%. The sample was degassed in several freeze-pump-thaw cycles before use.

2.1. FTIR smog chamber system at ford

Experiments were performed in a 140 liter Pyrex reactor connected to a Mattson Sirus 100 FTIR spectrometer [5]. The reactor was surrounded by 22 fluorescent black lamps (GE F40BLB), which were used to photochemically initiate the experiments. Experiments were performed at 296 ± 1 K in 700 Torr of air or N_2 diluent. The IR spectra were derived from 32 co-added interferograms with a spectral resolution of 0.25 cm^{-1} and an analytical path length of 27.6 m. Reactant and reference compounds were monitored using absorption features over the following wavenumber ranges: C_2H_2, 650–800 cm^{-1}; C_2H_4, 900–1000 cm^{-1}; *cis*-$CF_3CH{=}CHCl$, 850–890 cm^{-1}.

CH_3ONO was synthesized by drop-wise addition of concentrated H_2SO_4 to a saturated solution of $NaNO_2$ in methanol and was devoid of any detectable impurities using FTIR analysis. All other reagents were obtained from commercial sources at purities >99%.

2.2. FTIR photoreactor at University of Copenhagen

The CCAR photoreactor consists of a 101 liter quartz reactor connected to a Bruker IFS 66 v/s FTIR spectrometer [6]. Experiments were performed at 296 ± 1 K in 700 Torr of air diluent. The IR spectra were derived from 64 co-added interferograms with a spectral resolution of 0.25 cm^{-1} and an analytical path length between 50.01 and 53.42 m. Reactant and reference compounds were monitored using absorption features over the following wavenumber ranges: C_2H_2, 650–800 cm^{-1}; C_2H_4, 900–1000 cm^{-1}; *cis*-$CF_3CH{=}CHCl$, 850–890 and 1610–1670 cm^{-1}; O_3, 2720–2785 cm^{-1}.

Ozone was produced using a commercially available ozone generator from O_3-Technology. The ozone was preconcentrated using a silica gel trap, reducing the amount of O_2 introduced into the chamber. All other reagents were obtained from commercial sources at purities >99%.

3. Results and discussion

3.1. Relative rate study of Cl + cis-$CF_3CH{=}CHCl$

The rate of reaction (6) was measured relative to reactions (7) and (8):

$$Cl + cis\text{-}CF_3CH{=}CHCl \rightarrow \text{Products} \quad (6)$$

$$Cl + C_2H_4 \rightarrow \text{Products} \quad (7)$$

$$Cl + C_2H_2 \rightarrow \text{Products} \quad (8)$$

The initial mixtures consisted of 4.41–15.8 mTorr *cis*-$CF_3CH{=}CHCl$, 58.8–106 mTorr Cl_2 and either 4.17–6.69 mTorr C_2H_4 or 4.41–4.85 mTorr C_2H_2 in a total pressure of 700 Torr air or N_2 diluent. The loss of *cis*-$CF_3CH{=}CHCl$ is plotted against the loss

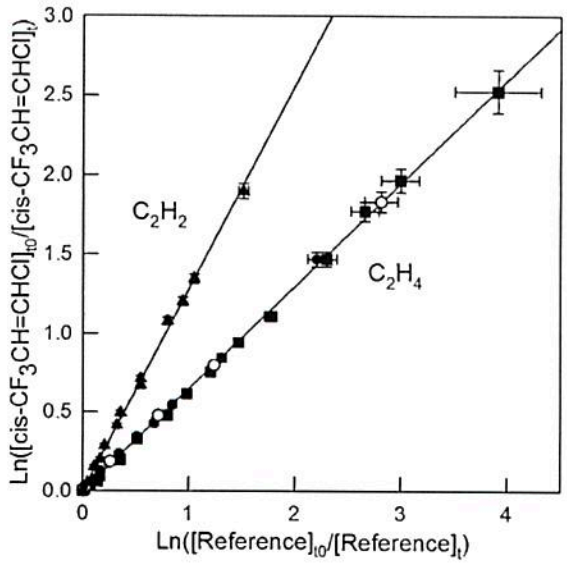

Figure 1. Loss of *cis*-$CF_3CH{=}CHCl$ relative to C_2H_4 (squares and circles) and C_2H_2 (triangles) in the presence of chlorine atoms in 700 Torr total pressure of air (solid symbols) or N_2 (open symbols), 296 ± 1 K. Experiments were performed at Ford (triangles and circles) and CCAR (squares). The error bars reflect the uncertainty in the determination of the reactant concentrations.

of the reference compound in Figure 1. Indistinguishable results were obtained from experiments performed in air and N_2 diluent.

Linear least squares analysis of the data in Figure 1 gives $k_6/k_7 = 0.65 \pm 0.04$ and $k_6/k_8 = 1.28 \pm 0.08$. Using $k_7 = (9.29 \pm 0.51) \times 10^{-11}$ and $k_8 = (5.07 \pm 0.34) \times 10^{-11}$ [7] gives $k_6 = (6.03 \pm 0.48) \times 10^{-11}$ and $(6.49 \pm 0.61) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, respectively. The fact that consistent values of k_6 were derived from experiments using different reference compounds suggests the absence of significant systematic errors in the present work. We choose to quote a final value for k_6 which is the average of the individual determinations together with uncertainties that encompass the extremes of the two individual determinations, hence, $k_6 = (6.26 \pm 0.84) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

This is the first study of the reaction of chlorine atoms with *cis*-$CF_3CH{=}CHCl$. We have previously studied the reactivity of chlorine atoms toward *trans*-$CF_3CH{=}CHCl$. The rate coefficient ratios measured for the *trans* isomer using C_2H_4 and C_2H_2 references were approximately 10% smaller [8] than those measured here showing that the *cis* isomer is slightly more reactive than the *trans* isomer toward chlorine atoms. This difference may be explained by steric hindrance.

3.2. Relative rate study of OH + *cis*-$CF_3CH{=}CHCl$

The kinetics of reaction (9) were measured relative to reactions (10) and (11):

$$OH + \textit{cis}\text{-}CF_3CH{=}CHCl \rightarrow \text{Products} \quad (9)$$

$$OH + C_2H_4 \rightarrow \text{Products} \quad (10)$$

$$OH + C_2H_2 \rightarrow \text{Products} \quad (11)$$

Initial reaction mixtures consisted of 58.5–63.2 mTorr *cis*-$CF_3CH{=}CHCl$, 108–205.7 mTorr CH_3ONO, and 7.05–7.35 mTorr C_2H_4 or 4.26–7.35 mTorr C_2H_2, and 0–14.7 mTorr NO in a total pressure of 700 Torr air and N_2 diluent. Figure 2 shows the loss of *cis*-$CF_3CH{=}CHCl$ plotted as a function of the loss of the reference compound.

Linear least squares analysis of the data in Figure 2 gives $k_9/k_{10} = 0.129 \pm 0.016$ and $k_9/k_{11} = 1.01 \pm 0.07$. We have shown

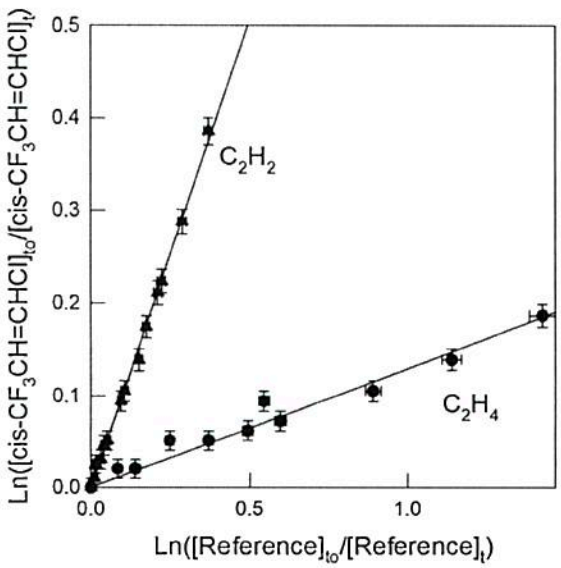

Figure 2. Loss of *cis*-$CF_3CH{=}CHCl$ relative to C_2H_4 (circles) and C_2H_2 (triangles) in the presence of OH radicals in 700 Torr total pressure of air and N_2, 296 ± 1 K. The error bars reflect the uncertainty in the determination of the reactant concentrations.

that Cl atoms are released during the OH initiated oxidation of $CF_3CH{=}CHCl$ [9]:

$$CF_3CHCH(OH)Cl + M \rightarrow Cl + CF_3CH{=}CH(OH) + M \quad (12)$$

The Cl atoms will react with *cis*-$CF_3CH{=}CHCl$ and pose a challenge for the OH relative rate measurement of k_9. Ideally, to minimize such complications a competitor would be added to the reaction mixtures to scavenge the Cl atoms. Alkanes, such as C_2H_6, are often used as chlorine atom scavengers but are not suitable for use in the present experiments because their reactivity toward OH radicals is comparable to that of *cis*-$CF_3CH{=}CHCl$ and hence would scavenge both chlorine atoms and OH radicals. To account for additional loss of *cis*-$CF_3CH{=}CHCl$ in the OH relative rate experiments caused by Cl atoms the system was modeled numerically. A model was constructed which incorporated the concentrations of *cis*-$CF_3CH{=}CHCl$, C_2H_4, and C_2H_2 used in the experiments, values of k_6–k_8 and k_9–k_{11} given above, and a chlorine atom yield of 40% from OH radical initiated oxidation as found for *trans*-$CF_3CH{=}CHCl$ [9]. The value of k_9 in the model was iterated starting with an uncorrected value, computing a correction, and then using the corrected value in the model to reevaluate the correction. The correction was larger for the experiments using C_2H_4 as reference than for those using C_2H_2 as reference. This reflects the fact that there is an approximately 5-fold difference in the rate coefficient ratios k_6/k_7 and k_9/k_{10}, while there is only approximately 10% difference in the rate coefficient ratios k_6/k_8 and k_9/k_{11}. The corrections applied to the C_2H_4 data were approximately 20% while those to the C_2H_2 data were approximately 5%. Correcting for the impact of chlorine atoms and propagating an additional 5% uncertainty to account for uncertainties in the correction procedure gives $k_9/k_{10} = 0.103 \pm 0.014$ and $k_9/k_{11} = 0.960 \pm 0.082$.

Using $k_{10} = 8.52 \times 10^{-12}$ [10] and $k_{11} = 8.45 \times 10^{-13}$ [11] gives $k_9 = (8.78 \pm 1.19) \times 10^{-13}$ and $(8.11 \pm 0.69) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. The fact that consistent values of k_9 were derived from experiments using different reference compounds suggests the absence of significant systematic errors in the present work. We choose to quote a final value for k_9, which is the average of the individual determinations with uncertainties that encompass the extremes of the individual determinations, hence, $k_9 = (8.45 \pm 1.52) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. This result is consistent with the value of $(9.46 \pm 0.22) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} reported by Gierczak et al. [12].

3.3. Relative rate study of OH + *trans*-$CF_3CH{=}CHCl$

We have previously conducted a relative rate study of the kinetics of the reaction of OH radicals with *trans*-$CF_3CH{=}CHCl$ using C_2H_4 and C_2H_2 as references and reported rate coefficient ratios of $k_{13}/k_{10} = 0.053 \pm 0.003$ and $k_{13}/k_{11} = 0.506 \pm 0.031$ [8].

$$OH + \textit{trans}\text{-}CF_3CH{=}CHCl \rightarrow \text{Products} \quad (13)$$

As discussed above, the formation of chlorine atoms is an unavoidable complication in relative rate studies of the reaction of OH radicals with $CF_3CH{=}CHCl$. To compute corrections to account for chlorine chemistry in the OH experiments a model was constructed which incorporated the concentrations of *trans*-$CF_3CH{=}CHCl$, C_2H_4, and C_2H_2 used in the previous experiments, values of k_6, k_7, k_8, k_{10}, k_{11}, and k_{13}, and a chlorine atom yield of 40% from OH radical initiated oxidation of *trans*-$CF_3CH{=}CHCl$. The corrections applied to the C_2H_4 data were approximately 20% while those for the C_2H_2 data were approximately 15%. Correcting for the impact of chlorine atoms and propagating an addition 5% uncertainty to account for uncertainties in the correction procedure gives $k_{13}/k_{10} = 0.042 \pm 0.004$ and $k_{13}/k_{11} = 0.430 \pm 0.034$. Using $k_{10} = 8.52 \times 10^{-12}$ [10] and $k_{11} = 8.45 \times 10^{-13}$ [11] gives $k_{13} = (3.58 \pm 0.34) \times 10^{-13}$ and

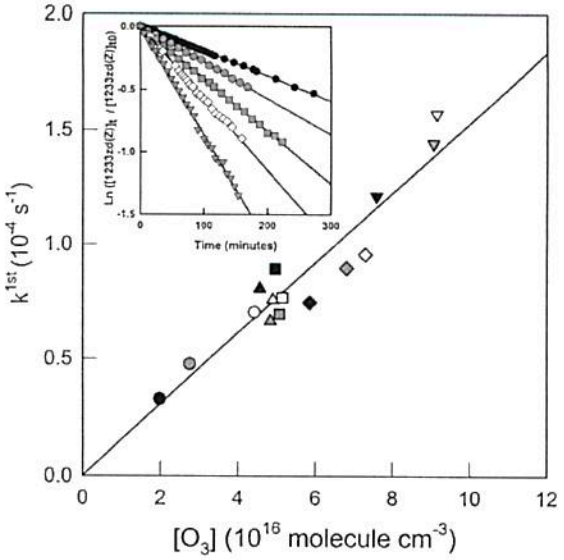

Figure 3. Pseudo-first order loss of *cis*-$CF_3CH{=}CHCl$ versus O_3 concentration. All data were obtained at CCAR. The inset shows the data obtained for 0.61, 0.85, 1.6, 2.3, and 2.80 Torr of O_3 in 700 Torr total pressure of air diluent, 295 ± 1 K.

$(3.63 \pm 0.29) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}, respectively. We choose to quote a final value for k_{13}, which is the average of the individual determinations with uncertainties that encompass the extremes of the individual determinations, hence, $k_{13} = (3.61 \pm 0.37) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}. This value is in agreement with the value of $(3.76 \pm 0.06) \times 10^{-13}$ (296 K) reported by Gierczak et al. [12] and the value of $(3.29 \pm 0.10) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} (298 K) reported by Orkin et al. [13]. Interestingly, the *trans* isomer is approximately a factor of 2 less reactive than the *cis* isomer toward OH radicals. An investigation of the significant difference between the rate coefficients for the *trans* and the *cis* isomer could be performed with a computational study, but is beyond the scope of the present study.

3.4. Absolute rate of O_3 + *cis*-$CF_3CH{=}CHCl$

The kinetics of reaction (5) were studied by observing the decay of *cis*-$CF_3CH{=}CHCl$ when exposed to O_3 in the reaction chamber at CCAR:

$$O_3 + \textit{cis}\text{-}CF_3CH{=}CHCl \rightarrow \text{Products} \qquad (5)$$

Cyclohexane was added to the reaction mixture as OH scavenger to avoid potential problems associated with the loss of *cis*-$CF_3CH{=}CHCl$ via reaction with OH radicals formed in reaction (5) [10]. Initial reaction mixtures consisted of 4.07–4.17 mTorr *cis*-$CF_3CH{=}CHCl$, 3.96–31.79 mTorr cyclohexane, and 0.61–2.82 Torr O_3 in a total pressure of 700 Torr air diluent. Variation in the [cyclohexane]/[*cis*-$CF_3CH{=}CHCl$] ratio over the range of 0.9–7.6 had no discernable effect on the observed decay of *cis*-$CF_3CH{=}CHCl$ suggesting that loss via reaction with OH radicals is not a significant complication.

The loss of *cis*-$CF_3CH{=}CHCl$ followed pseudo first-order kinetics in all experiments. The insert in Figure 3 shows the data obtained for 0.61, 0.85, 1.6, 2.3, and 2.80 Torr of O_3. A plot of the pseudo first-order decay of *cis*-$CF_3CH{=}CHCl$ versus O_3 concentration is shown in Figure 3. A linear least squares fit gives $k_5 = (1.53 \pm 0.09) \times 10^{-21}$ cm^3 $molecule^{-1}$ s^{-1}. We choose to cite a final value for k_5 with error limits which include two standard deviations from the least squares regression and a propagated 5% uncertainty in the O_3 calibration, of $k_5 = (1.53 \pm 0.12) \times 10^{-21}$ cm^3 $molecule^{-1}$ s^{-1}.

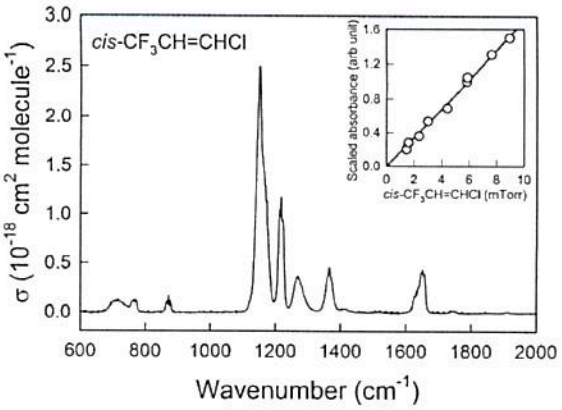

Figure 4. IR spectrum of *cis*-$CF_3CH{=}CHCl$ in 700 Torr of air at 295 K (Ford).

This is the first study of the reaction of O_3 with *cis*-$CF_3CH{=}CHCl$. We have previously reported a value of $(1.46 \pm 0.12) \times 10^{-21}$ cm^3 $molecule^{-1}$ s^{-1} for the *trans* isomer, *trans*-$CF_3CH{=}CHCl$ [8]. The reactivities of *cis*- and *trans*-$CF_3CH{=}CHCl$ toward O_3 are indistinguishable.

3.5. Infrared spectrum of *cis*-$CF_3CH{=}CHCl$

IR spectra were obtained by expanding known volumes of *cis*-$CF_3CH{=}CHCl$ into the chambers and recording spectra for different concentrations of *cis*-$CF_3CH{=}CHCl$. The IR spectra obtained at Ford and CCAR were in good agreement (within 5%). Below and in the following sections, we proceed using the spectrum obtained at Ford. Figure 4 shows the IR spectrum of *cis*-$CF_3CH{=}CHCl$ recorded in 700 Torr air diluent at 296 ± 1 K. As seen from the inset in Figure 4 the intensity of the absorption features increased linearly with the *cis*-$CF_3CH{=}CHCl$ concentration. The integrated absorption cross-section of *cis*-$CF_3CH{=}CHCl$ (600–2000 cm^{-1}) is $(1.48 \pm 0.07) \times 10^{-16}$ cm $molecule^{-1}$. Gierczak et al. [12] report a value of $(1.60 \pm 0.01) \times 10^{-16}$ cm $molecule^{-1}$ which is consistent with our measurement within the expected combined experimental uncertainties.

4. Implications for atmospheric chemistry

The present work improves our understanding of the atmospheric chemistry of *cis*-$CF_3CH{=}CHCl$. Cl atoms, OH radicals, and O_3 react with *cis*-$CF_3CH{=}CHCl$ with rate coefficients of $(6.26 \pm 0.84) \times 10^{-11}$, $(8.45 \pm 1.52) \times 10^{-13}$, and $(1.53 \pm 0.12) \times 10^{-21}$ cm^3 $molecule^{-1}$ s^{-1}, respectively. Organic compounds are removed from the atmosphere via photolysis, wet and dry deposition, and gas-phase reaction with OH radicals, O_3, and Cl atoms. *cis*-$CF_3CH{=}CHCl$ does not absorb at wavelengths greater than 200 nm and is volatile and hence will not be lost via photolysis or wet or dry deposition to any appreciable extent [14]. The value of k(OH + *cis*-$CF_3CH{=}CHCl$) derived in the present work can be used to provide an estimate of the atmospheric lifetime of *cis*-$CF_3CH{=}CHCl$. Using a global tropospheric 24 h average OH concentration of 1.0×10^6 molecule cm^{-3} [15] gives an estimated lifetime with respect to reaction with OH radicals of 14 days. The approximate nature of this lifetime should be stressed. The average daily concentration of OH radicals in the atmosphere varies significantly with location and season [16] and local atmospheric lifetimes of *cis*-$CF_3CH{=}CHCl$ will vary similarly.

Our value for k(O_3 + *cis*-$CF_3CH{=}CHCl$) can be combined with the global background concentration of O_3 of approximately 35 ppb

[17] to provide an estimate of the atmospheric lifetime of *cis*-$CF_3CH{=}CHCl$ with respect to reaction with O_3 of 24 years, which is clearly of minor importance compared to the OH reaction pathway. Reaction with Cl atoms is a negligible fate for *cis*-$CF_3CH{=}CHCl$ as the atmospheric concentration of Cl atoms is generally low [17]. Assuming a global average Cl atom concentration of 10^3 cm^{-3} we derive a lifetime with respect to Cl atom reaction of 6 months. We proceed on the assumption that the atmospheric lifetime of *cis*-$CF_3CH{=}CHCl$ is dictated by reaction with OH radicals and is approximately 14 days.

The radiative efficiency for *cis*-$CF_3CH{=}CHCl$ calculated using the method of Pinnock et al. [18] and the IR spectrum in Figure 4 was 0.19 W m^{-2} ppb^{-1}. For short-lived compounds, such as *cis*-$CF_3CH{=}CHCl$, non-uniform horizontal and vertical mixing in the atmosphere need to be taken into account. Hodnebrog et al. [19] provide a correction factor of relative efficiencies for very short-lived compounds (Eq. (II)) that accounts for non-uniform horizontal and vertical mixing:

$$f(\tau) = \frac{a\tau^b}{1 + c\tau^d} \tag{II}$$

where τ is the lifetime of *cis*-$CF_3CH{=}CHCl$, a, b, c, and d are constants with values of 2.962, 0.9312, 2.994, and 0.9302, respectively. Using $\tau = 0.038$ years gives $f(\tau) = 0.122$. Hence we arrive at a final value of *cis*-$CF_3CH{=}CHCl$ of 0.0231 W m^{-2} ppb^{-1}.

Using Eq. (III) the global warming potential (GWP) can be calculated:

$$\mathrm{GWP}\left(x(t')\right) = \frac{\int_0^{t'} F_x \exp\left(-t/\tau_x\right) dt}{\int_0^{t'} F_{CO_2} R(t) dt} \tag{III}$$

where F_{CO_2} is the radiative efficiency of CO_2, $R(t)$ is the response function that describes the decay of an instantaneous pulse of CO_2, F_x is the radiative efficiency of *cis*-$CF_3CH{=}CHCl$, and τ_x is its atmospheric lifetime. The denominator in Eq. (III) is the absolute global warming potential (AGWP) for CO_2. Using the IPCC AR5 F_{CO_2} of 1.7517×10^{-15} W m^{-2} kg^{-1} [20] with the time-integrated airborne CO_2 fractions evaluated by Joos et al. [21] for different time horizons, we arrive at AGWPs for CO_2 of 0.194, 0.715 and 2.512 W m^{-2} ppb^{-1} for 20, 100, and 500 year time horizons, respectively.

Using the radiative efficiency of 0.0231 W m^{-2} ppb^{-1} and atmospheric lifetime of 14 days, GWP values for *cis*-$CF_3CH{=}CHCl$ are estimated to 2, 0, and 0, for 20, 100, and 500 year horizons respectively. Gierczak et al. report a GWP_{100} value of approximately 3 [12] which is consistent with our result. *cis*-$CF_3CH{=}CHCl$ has a negligible GWP and will not make a significant contribution to radiative forcing of climate change. Patten and Wuebbles [22] conducted a modeling study and derived an ozone depleting potential (ODP) for *trans*-$CF_3CH{=}CHCl$ of 0.00034. The atmospheric lifetime of *cis*-$CF_3CH{=}CHCl$ is approximately half that of the *trans* isomer and hence the ODP for *cis*-$CF_3CH{=}CHCl$ will be even lower than for *trans*-$CF_3CH{=}CHCl$. We conclude that *cis*-$CF_3CH{=}CHCl$ will make negligible contributions to stratospheric ozone depletion and to radiative forcing of climate change.

Acknowledgements

We acknowledge financial support from the Villum Kann Rasmussen Foundation and EUROCHAMP2.

References

[1] M.J. Molina, F.S. Rowland, Nature 249 (1974) 810.
[2] J.D. Farman, B.G. Gardiner, J.D. Shanklin, Nature 315 (1985) 207.
[3] T.J. Wallington, W.F. Schneider, J. Sehested, O.J. Nielsen, J. Chem. Soc. Faraday Discuss. 100 (1995) 55.
[4] T.J. Wallington, S.M. Japar, J. Atmos. Chem. 9 (1989) 399.
[5] T.J. Wallington, C.A. Gierczak, J.C. Ball, S.M. Japar, Int. J. Chem. Kinet. 21 (1989) 1077.
[6] E.J.K. Nilsson, C. Eskebjerg, M.S. Johnson, Atmos. Environ. 43 (2009) 3029.
[7] T.J. Wallington, J.M. Andino, I.M. Lokovic, E.W. Kaiser, G. Marston, J. Phys. Chem. 94 (1990) 3644.
[8] M.P. Sulbaek Andersen, E.J.K. Nilsson, O.J. Nielsen, M.S. Johnson, M.D. Hurley, T.J. Wallington, J. Photochem. Photobiol. A: Chem. 199 (2008) 92.
[9] M.P. Sulbaek Andersen, O.J. Nielsen, M.D. Hurley, T.J. Wallington, Phys. Chem. Chem. Phys. 14 (2012) 1735.
[10] J.G. Calvert, R. Atkinson, J.A. Kerr, S. Madronich, G.K. Moortgat, T.J. Wallington, G. Yarwood, The Mechanisms of Atmospheric Oxidation of the Alkenes, Oxford University Press, Oxford, 2000.
[11] M. Sørensen, E.W. Kaiser, M.D. Hurley, T.J. Wallington, O.J. Nielsen, Int. J. Chem. Kinet. 35 (2003) 191.
[12] T. Gierczak, M. Baasandorj, J.B. Burkholder, J. Phys. Chem. A 118 (2014) 11015.
[13] V.L. Orkin, L.E. Martynova, M.J. Kurylo, J. Phys. Chem. A 118 (2014) 5263.
[14] Honeywell Material Data Safety Sheet for HCFO-1233zd. http://msds-resource.honeywell.com/ (downloaded April 2015).
[15] R.G. Prinn, J. Huang, R.F. Weiss, D.M. Cunnold, P.J. Fraser, P.G. Simmonds, A. McCulloch, C. Harth, P. Salameh, S. O'Doherty, R.H.J. Wang, L. Porter, B.R. Miller, Science 292 (2001) 1882.
[16] World Meteorological Organization (WMO), Scientific Assessment of Ozone Depletion: 2010, Global Ozone, Research and Monitoring Project – Report 52, Geneva, Switzerland, 2011.
[17] B.J. Finlayson-Pitts, J.N. Pitts Jr., Chemistry of the Upper and Lower Atmosphere, Academic Press, London, 2000.
[18] S. Pinnock, M.D. Hurley, K.P. Shine, T.J. Wallington, T.J. Smyth, J. Geophys. Res.: Atmos. 100 (1995) 23227.
[19] Ø. Hodnebrog, M. Etminan, J.S. Fuglestvedt, G. Marston, G. Myhre, C.J. Nielsen, K.P. Shine, T.J. Wallington, Rev. Geophys. 51 (2013) 300.
[20] G. Myhre, D. Shindell, F.-M. Bréon, W. Collins, J. Fuglestvedt, J. Huang, D. Koch, J.-F. Lamarque, D. Lee, B. Mendoza, T. Nakajima, A. Robock, G. Stephens, T. Takemura, H. Zhang, in: T.F. Stocker, D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex, P.M. Midgley (Eds.), Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change., 2013.
[21] F. Joos, R. Roth, J.S. Fuglestvedt, G.P. Peters, I.G. Enting, W. von Bloh, V. Brovkin, E.J. Burke, M. Eby, N.R. Edwards, T. Friedrich, T.L. Frölicher, P.R. Halloran, P.B. Holden, C. Jones, T. Kleinen, F.T. Mackenzie, K. Matsumoto, M. Meinshausen, G.K. Plattner, A. Reisinger, J. Segschneider, G. Shaffer, M. Steinacher, K. Strassmann, K. Tanaka, A. Timmermann, A.J. Weaver, Atmos. Chem. Phys. 13 (2013) 2793.
[22] K.O. Patten, D.J. Wuebbles, Atmos. Chem. Phys. 10 (2010) 10867.

UNIVERSITY OF CALIFORNIA, RIVERSIDE

BERKELEY • DAVIS • IRVINE • LOS ANGELES • RIVERSIDE • SAN DIEGO • SAN FRANCISCO SANTA BARBARA • SANTA CRUZ

COLLEGE OF ENGINEERING - 022
CENTER FOR ENVIRONMENTAL RESEARCH & TECHNOLOGY
(951) 781-5791 FAX (951) 781-5790

RIVERSIDE, CALIFORNIA 92521-0434

March 9, 2017

To: Whom It May Concern

From: William P. L. Carter
Consultant in Atmospheric Chemistry and Reactivity, and
Research Chemist, Emeritus
College of Engineering Center for Environmental Research and Technology
University of California, at Riverside

Re: Estimation of Ground Level Atmospheric Ozone Impacts of *Cis* 1-Chloro-3,3,3-Trifluoropropene

Background

Ozone in photochemical smog is formed from the gas-phase reactions of volatile organic compounds (VOCs) and oxides of nitrogen (NO_x) in sunlight, and control of both VOCs and NO_x is required to attain air quality standards for ground-level ozone. Many different types of VOCs are emitted into the atmosphere, each reacting with different rates and mechanisms and therefore with different impacts on ground level ozone formation. In recognition of this, the U.S. EPA has exempted from regulations as VOC ozone precursors certain volatile organic compounds whose ozone impacts were expected to be less than ethane (Dimitriades, 1999; RRWG, 1999a, EPA, 2005), In addition, California has adopted regulations with reactivity-based adjustments for several types of VOC sources (CARB 1993, 2000). Although ozone impacts can be quantified in different ways (RRWG, 1999; Hales, 2007), the most commonly used method is the "incremental reactivity" of the compound, which is the amount of additional ozone formed when a small amount of a VOC is emitted into a standard environment, divided by the amount emitted (Carter and Atkinson, 1989). Although incremental reactivities will depend on the environment where the compound is emitted, the Maximum Incremental Reactivity (MIR) scale developed by the author (Carter, 1994, 2010) represents the impacts under conditions where ozone is most sensitive to VOC emissions, and is used in the current reactivity-based regulations implemented in California. This scale, together with other reactivity scales developed by the author (Carter, 1994, 2010), has also been used by the U.S. EPA as a basis of comparing the ozone impacts of compounds relative to ethane for the purpose of making VOC exemption decisions.

Halogenated propenes such as *cis* and *trans* 1-chloro-3,3,3-trifluoropropene ($CF_3CH=CHCl$) are compounds of interest whose use and manufacture may result in their being emitted into the atmosphere, where they may react to promote ground-level ozone formation. This will result in these compounds being subject to VOC regulations aimed at reducing ozone formation, which may adversely impact their production costs and marketability. Because of the interest in *trans* 1-chloro-3,3,3-trifluoropropene, we previously carried out an experimental and modeling study of the ozone impacts of this compound, and the results are described in a detailed report that is available online (Carter, 2009a). Briefly, this work consisted of deriving an atmospheric reaction mechanism for this compound based on available data in the literature and various estimates, conducting environmental chamber experiments to test and verify the predictive capability of the mechanism with respect to factors affecting ozone formation, and using the

mechanism in models used to calculate the MIR and other reactivity scales to calculate its ozone impact, and comparing the results with those for ethane and other compounds that were previously calculated and used in regulatory applications. The average ratio of mass-based incremental reactivities relative to ethane for all the box model scenarios was found to be 0.19±0.03 and the MIR ratio was 0.16±0.02, where the uncertainty ranges reflect the variability among the various model scenarios. It is concluded that if ethane is used as the standard to define "negligible" ozone impact for the purpose of determining VOC exemptions for ozone precursors, then trans 1-chloro-3,3,3-trifluoropropene will meet this standard. Trans 1-chloro-3,3,3-trifluoropropene was also found to have no significant effect on particle formation in the incremental reactivity chamber experiments

Ozone Impact of *Cis* 1-Chloro-3,3,3-Trifluoropropene

We have not previously studied the ozone impact of the *cis* isomer of this compound, which is also of interest. Although we expect the mechanisms for the atmospheric reactions for the two isomers to be very similar, with the expected radical intermediates and oxidation products formed when they react being essentially the same, there are differences in how fast they react in the atmosphere, and this will affect their ozone impacts. The main initial atmospheric reaction of these halopropenes is reaction with the OH radical. Reaction with ozone also needs to be considered when assessing ozone impacts of unsaturated compounds, but the measured rate constants for these halopropenes are too low for this to be an important loss process for them in the atmosphere. The available information concerning these rate constants is as follows (with rate constants given in units of cm^3 $molec^{-1}$ s^{-1}):

Isomer	OH Reaction	O_3 Reaction	Reference
Trans	4.40×10^{-13}	1.46×10^{-21}	Sulbaek Andersen et al (2008)
	3.61×10^{-13}		Løffler Andersen et al (2015)
Cis	8.45×10^{-13}	1.53×10^{-21}	Løffler Andersen et al (2015)

Our previous study of the trans isomer (Carter, 2009a) used the earlier OH rate constant of Sulbaek Andersen et al (2008), which is slightly higher than the more recent measurement of Løffler Andersen et al (2015) that included corrections for effects of unwanted Cl chemistry. Therefore, if we were to recalculate the reactivity values for the trans isomer using the newer rate constant, they would be slightly lower, but the conclusion that it is much less reactive than ethane would obviously not be affected.

For relatively slowly reacting compounds such as these halopropenes, the amount they react in the one-day scenarios to calculate the MIR and other Carter reactivity scales (Carter, 1994, 2010) is approximately proportional to how fast they react, which for these compounds is determined by their OH rate constant. This means that if all other aspects of the mechanisms are similar, as is expected to be the case if the only difference is the *cis* vs. *trans* configuration, then the ratios in the reactivities would be approximately proportional to the ratios in their OH rate constants. Since the *cis* isomer has an OH rate constant that is 1.9 times higher than used by Carter (2009) to calculate the reactivities of the *trans* isomer, then the reactivities for the *cis* isomer should be approximately than those given by Carter (2009) for the *trans* isomer, multiplied by 1.9. That means that we estimate that the ozone impact of the *cis* isomer relative to ethane for all the box model scenarios to be 0.36±0.06 and the MIR ratio to be 0.30±0.04. Although the ozone impact for the *cis* isomer is estimated to be about twice that for the *trans* isomer, it is still about three times less than that for ethane on a mass basis.

Conclusions

Although we did not conduct environmental chamber experiments to test the ability of mechanism we previously developed for the *trans* isomer to predict the reactivity of the *cis* isomer if the increased OH rate constant is used, we have every reason to expect that the results will be similar to those we obtained when testing mechanisms for the three other halopropenes we have studied experimentally (Carter 2009a-c). It is therefore concluded that if ethane is used as the standard to define "negligible" ozone impact for the purpose of determining VOC exemptions for ozone precursors, then *cis* 1-chloro-3,3,3-trifluoropropene will meet this standard.

References

CARB (1993): "Proposed Regulations for Low-Emission Vehicles and Clean Fuels -- Staff Report and Technical Support Document," California Air Resources Board, Sacramento, CA, August 13, 1990. See also Appendix VIII of "California Exhaust Emission Standards and Test Procedures for 1988 and Subsequent Model Passenger Cars, Light Duty Trucks and Medium Duty Vehicles," as last amended September 22, 1993. Incorporated by reference in Section 1960.

CARB (2000): "Initial Statement of Reasons for the Proposed Amendments to the Regulation for Reducing Volatile Organic Compound Emissions from Aerosol Coating Products and Proposed Tables of Maximum Incremental Reactivity (MIR) Values, and Proposed Amendments to Method 310, 'Determination of Volatile Organic Compounds in Consumer Products'," California Air Resources Board, Sacramento, CA, May 5.

Carter, W. P. L. and R. Atkinson (1989): "A Computer Modeling Study of Incremental Hydrocarbon Reactivity", Environ. Sci. Technol., 23, 864.

Carter, W. P. L. (1994): "Development of Ozone Reactivity Scales for Volatile Organic Compounds," J. Air & Waste Manage. Assoc., 44, 881-899.

Carter, W. P. L (2010): "Updated Maximum Incremental Reactivity Scale and Hydrocarbon Bin Reactivities for Regulatory Applications," Report to the California Air Resources Board, Contract 07-339, January 28, available at http://www.cert.ucr.edu/~carter/SAPRC/MIR10.pdf.

Carter, W. P. L. (2009a): "Investigation of Atmospheric Ozone Impacts of 1-chloro-3,3,3-Trifluoropropene," Final Report to Honeywell International Inc, June 8. Available at http://www.cert.ucr.edu/~carter/absts.htm#ZDErept.

Carter, W. P. L. (2009b). "Investigation of the Atmospheric Ozone Impacts of Trans 1,3,3,3-Tetrafluoropropene," Final Report to Honeywell International Inc. Contract UCR-09010016, February 9. Available at http://www.cert.ucr.edu/~carter/absts.htm #ZEErept.

Carter, W. P. L. (2009c). "Investigation of the Atmospheric Ozone Impacts of 2,3,3,3-Tetrafluoropropene," Final Report to Honeywell International Inc. Contract UCR-09010016, June 2. Available at http://www.cert.ucr.edu/~carter/absts.htm #YFrept.

Dimitriades, B. (1999): "Scientific Basis of an Improved EPA Policy on Control of Organic Emissions for Ambient Ozone Reduction," J. Air & Waste Manage. Assoc. 49, 831-838

EPA (2005): "Interim Guidance on Control of Volatile Organic Compounds in Ozone State Implementation Plans," Federal Register, 70, 54046-54051, September 13.

Hales, J. M. (2007) "The Reactivity Research Working group: A Chronological Overview and Evaluation," Report to NARSTO, available at http://narsto.org/rrwg_reports.

Loffler Andersen, L., F. F. Østerstrøm., M. P. Sulbaek Andersen, O. J. Nielsen, and T. J. Wallington (2015): " Atmospheric chemistry of cis-CF_3CH CHCl (HCFO-1233zd(Z)): Kinetics of the gas-phase reactions with Cl atoms, OH radicals, and O_3," Chem Phys Lett. 639, 289-293.

RRWG (1999): "VOC Reactivity Policy White Paper", prepared by the Reactivity Research Working Group, October, 1999. Available at http://www.narsto.org/sites/narsto-dev.ornl.gov/files/VOCReactWhtPaper.pdf. See also other reports available at http://www.narsto.org/voc_reactivity.

Sulbaek Andersen, M.P., E.J.K. Nilsson, O.J. Nielsen, M.S. Johnson, M.D. Hurley, and T.J.Wallington (2008): "Atmospheric chemistry of trans-CF_3CH=CHCl: Kinetics of the gas-phase reactions with Cl atoms, OH radicals, and O_3," J. Photochem. Photobiol A. 199, 92-97.

Chemosphere 129 (2015) 135–141

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Atmospheric chemistry of short-chain haloolefins: Photochemical ozone creation potentials (POCPs), global warming potentials (GWPs), and ozone depletion potentials (ODPs)

T.J. Wallington [a,*], M.P. Sulbaek Andersen [b], O.J. Nielsen [c]

[a] System Analytics and Environmental Sciences Department, Ford Motor Company, Mail Drop RIC-2122, Dearborn, MI 48121-2053, USA
[b] Department of Chemistry and Biochemistry, California State University Northridge, 18111 Nordhoff St., Northridge, CA 91330-8262, USA
[c] Copenhagen Center for Atmospheric Research, Department of Chemistry, University of Copenhagen, Universitetsparken 5, 2100 Copenhagen, Denmark

HIGHLIGHTS

- Commercially relevant short-chain haloolefins will be released into the atmosphere.
- Haloolefins have short atmospheric lifetimes (a few days or weeks).
- Short-chain haloolefins degrade in the atmosphere giving HF, HCl, CO_2 and $CF_3C(O)OH$.
- The degradation products do not pose a significant risk to ecosystems.

ARTICLE INFO

Article history:
Received 1 April 2014
Received in revised form 26 June 2014
Accepted 27 June 2014
Available online 26 July 2014

Handling Editor: I. Cousins

Keywords:
Hydrofluoroolefins
Atmospheric chemistry
Global warming potential (GWP)
Photochemical ozone creation potential (POCP)
Ozone depletion potential (ODP)

ABSTRACT

Short-chain haloolefins are being introduced as replacements for saturated halocarbons. The unifying chemical feature of haloolefins is the presence of a >C=C< double bond which causes the atmospheric lifetimes to be significantly shorter than for the analogous saturated compounds. We discuss the atmospheric lifetimes, photochemical ozone creation potentials (POCPs), global warming potentials (GWPs), and ozone depletion potentials (ODPs) of haloolefins. The commercially relevant short-chain haloolefins $CF_3CF{=}CH_2$ (1234yf), *trans*-$CF_3CH{=}CHF$ (1234ze(Z)), $CF_3CF{=}CF_2$ (1216), *cis*-$CF_3CH{=}CHCl$ (1233zd(Z)), and *trans*-$CF_3{-}CH{=}CHCl$ (1233zd(E)) have short atmospheric lifetimes (days to weeks), negligible POCPs, negligible GWPs, and ODPs which do not differ materially from zero. In the concentrations expected in the environment their atmospheric degradation products will have a negligible impact on ecosystems. $CF_3CF{=}CH_2$ (1234yf), *trans*-$CF_3CH{=}CHF$ (1234ze(Z)), $CF_3CF{=}CF_2$ (1216), *cis*-$CF_3CH{=}CHCl$ (1233zd(Z)), and *trans*-$CF_3{-}CH{=}CHCl$ (1233zd(E)) are environmentally acceptable.

1. Introduction

Recognition of the adverse environmental impact of chlorofluorocarbon (CFC) release into the atmosphere (Molina and Rowland, 1974; Farman et al., 1985) has led to a sustained international effort to replace these compounds with environmentally acceptable alternatives. Short-chain haloolefins have recently been developed to replace CFCs and saturated hydrofluorocarbons in air conditioning units (Brown, 2009). For example, $CF_3CF{=}CH_2$ (HFO-1234yf) is under consideration as a replacement for CF_3CHF_2 (HFC-134a) in vehicle air conditioning units (Brown, 2009). As listed in Table 1, *trans*-$CF_3CH{=}CHF$ (HFO-1234ze(E)), $CF_3CF{=}CF_2$ (FO-1216), *cis*-$CF_3CH{=}CHCl$ (HCFO-1233zd(Z)), and *trans*-$CF_3{-}CH{=}CHCl$ (HCFO-1233zd(E)) are also finding commercial applications. These haloalkenes are volatile and hydrophobic and following release into the environment will partition into the atmosphere. The $\log K_{ow}$ values for HFO-1234ze(E), HFO-1234yf, and HCFO-1233zd(E) of 1.6, 2.0, and 2.2, respectively (Singh, 2014), indicate that haloalkenes are not bioaccumulative (Bintein et al., 1993).

Prior to their large-scale industrial use an assessment of the atmospheric chemistry, and hence environmental impact, of haloolefins is needed. There is now a substantial database in the literature on this subject. We discuss the atmospheric chemistry of commercially relevant short-chain haloolefins. Four potential environmental impacts need to be considered: (i) tropospheric

* Corresponding author.
E-mail address: twalling@ford.com (T.J. Wallington).

http://dx.doi.org/10.1016/j.chemosphere.2014.06.092
0045-6535/

Table 1
Commercial applications of haloolefins.

Haloolefin	Applications
CF_3—CF=CH_2 (HFO-1234yf)	Refrigerant in vehicle AC systems
trans-CF_3—CH=CHF (HFO-1234ze(E))	Aerosol propellant, in expanded polystyrene (styrofoam) insulation industry, refrigerant
CF_3—CF=CF_2 (HFO-1216)	Co-monomer for FEP polymer, raw material for certain routes to make 1234yf
Z-CF_3—CH=CHCl (HCFO-1233zd(Z))	Degreasing of mechanical parts and dry cleaning
E-CF_3—CH=CHCl (HCFO-1233zd(E))	Polyurethane foam blowing agent gas when the insulation performance is critical, spray foam for building roof insulation

ozone formation, (ii) climate change, (iii) stratospheric ozone loss, and (iv) formation of noxious or toxic degradation products. For illustrative purposes, we provide detailed information for the atmospheric chemistry of $CF_3CF{=}CH_2$, highlighted above, and draw comparisons to analogous compounds within this particular chemical group and beyond.

2. Atmospheric lifetimes

Halocarbons are removed from the atmosphere by two general mechanisms; reaction with OH radicals and photolysis. Haloolefins are the subset of halocarbons which contain a $\rangle C{=}C\langle$ double bond. The reaction of OH radicals with $\rangle C{=}C\langle$ double bonds is very rapid and as a result dominates the atmospheric removal mechanism for haloolefins. The inclusion of one, or more, double bonds is a particularly effective method to increase the reactivity of organic molecules towards OH radicals. As an illustration we can compare the reactivity of $CF_3CF_2CH_3$ (HFC-245cb) and $CF_3CF{=}CH_2$ (HFO-1234yf). With respect to reaction with OH radicals $CF_3CF{=}CH_2$ is approximately 2000 times more reactive than $CF_3CF_2CH_3$ (WMO, 2011). Haloalkenes react with other gas phase oxidants present in the atmosphere such as O_3, Cl atoms, and NO_3 radicals but these reactions are of limited significance compared to that with OH radicals.

Uniform mixing of a gas in the atmosphere requires a time scale of years. The lifetimes of haloolefins are of the order of days and hence following their release they will not be well mixed in the atmosphere. For short lived compounds such as the haloolefins it is not possible to assign a unique atmospheric lifetime. The lifetimes depend on the location of emissions and the chemical and physical conditions of the atmosphere. The atmospheric lifetime of haloolefins emitted in the winter at high latitudes where there is little photochemical activity will be substantially longer than when emitted in the summer in the tropics. Nevertheless, it is useful to assign an approximate atmospheric lifetime to short lived species using representative average OH radical concentrations. For species with lifetimes <1 d an average daytime [OH] of 2.5×10^6 cm^{-3} is used together with the rate coefficient at 298 K (Calvert et al., 2011). For species with lifetimes between 1 d and 1 year a diurnally averaged [OH] of 1.0×10^6 cm^{-3} is used with the OH rate coefficient at 298 K (Calvert et al., 2011). For species with lifetimes >1 year mixing throughout the troposphere is assumed with an average [OH] of 1.0×10^6 cm^{-3} together with the OH rate coefficient at 272 K (Calvert et al. 2011).

The room temperature rate coefficients for reactions of OH radicals with the commercially significant haloolefins considered here are in the range $(0.4–2.0) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. The concentration of OH in the troposphere is highly variable but averages approximately 1.0×10^6 cm^{-3}. Combining the OH rate coefficient with the OH radical concentration provides a pseudo first order loss rate of approximately $(0.4–2.0) \times 10^{-6}$ s^{-1} or a lifetime range of approximately 6–30 d.

As seen from Table 2, haloolefins have longer atmospheric lifetimes than the corresponding alkenes but shorter lifetimes than the corresponding haloalkanes. These trends reflect the electrophilic addition of OH radicals to $\rangle C{=}C\langle$ double bonds. The electron withdrawing effect of the halogen atoms in haloolefins results in a reduction in reactivity compared to the alkenes. The presence of the reactive $\rangle C{=}C\langle$ double bond in haloolefins results in much lower lifetimes for these compounds than for haloalkanes. For example, $CF_3CF_2CH_3$ (HFC-245cb) has a lifetime of 47.1 years while CF_3CFCH_2 (HFC-1234yf) has a lifetime of 10.5 d.

3. Photochemical ozone creation potentials (POCPs)

The photochemical ozone creation potentials (POCPs) for a range of HFOs have been evaluated by Wallington et al. (2010) using the method outlined by Derwent et al. (1998) and Jenkin (1998). POCP is defined as the additional ozone formed in a multi-day modeling when adding a given amount of volatile organic compound relative to adding the *same mass* of ethene (Derwent et al. 1996). The POCP scale is relative with the POCP for ethene defined as 100. POCP values are determined over a period of approximately 5 d along an idealized straight line trajectory using a photochemical trajectory model. Running a photochemical trajectory model is challenging and is not a practical option for non-specialists in the field. Derwent et al. (1998) and Jenkin (1998) developed a simplified estimation procedure which uses fundamental molecular properties (molecular weight, number of reactive bonds, and rate coefficient for reaction with OH radicals) to provide estimated POCPs using the expression:

$$\varepsilon^{\mathrm{POCP}} = \alpha_1 \times \gamma_s \times \gamma_R^{\beta}(1 - \alpha_2 \times n_c) \quad (1)$$

where $\varepsilon^{\mathrm{POCP}}$ is the estimated POCP; α_1, α_2, and β are constants; γ_s is the structure based ozone formation index, γ_R is the reactivity based ozone formation index, and n_c is the carbon number of the compound. The structure and reactivity based ozone formation indices are further defined as:

$$\gamma_s = (n_B/M) \times (28/6) \quad (2)$$

$$\gamma_R = (k_{\mathrm{OH}}/n_B) \times (6/k_{\mathrm{OH}}^{\mathrm{ethene}}) \quad (3)$$

where n_B is the total number of C—C and C—H bonds in the molecule, M is the molecular weight, k_{OH} is the rate coefficient for reaction with OH radicals at 298 K and 760 Torr of air, and $k_{\mathrm{OH}}^{\mathrm{ethene}}$ is the rate coefficient for reaction of ethene with OH radicals at 298 K and 760 Torr of air (8.64×10^{-12} cm^3 molecule^{-1} s^{-1}, Jenkin (1998)).

POCPs for the commercially relevant haloolefins are listed in Table 2. As an example of the calculations, consider the case of Z-$CF_3CH{=}CHCF_3$ (HFO-1336Z) which has a molecular weight of 164, has 4 reactive bonds ($n_B = 4$), and reacts with OH radicals with a rate coefficient at 298 K of 4.9×10^{-13} cm^3 molecule^{-1} s^{-1} (Baasandorj et al., 2011). Substituting these values into Eqs. (2) and (3) gives $\gamma_s = 0.114$ and $\gamma_R = 0.085$. Combining the optimized parameters given in Table 2 of Jenkin (1998) with the rate coefficient for reaction of OH radicals with Z-$CF_3CH{=}CHCF_3$ gives $\alpha_1 = 111$, $\alpha_2 = 0.04$, and $\beta = 0.5$. Finally, Z-$CF_3CH{=}CHCF_3$ has four carbon atoms and hence $n_C = 4$. Substituting these values into Eq. (1) gives an estimated POCP for Z-$CF_3CH{=}CHCF_3$ of 3.1.

Table 2
Atmospheric lifetimes, photochemical ozone creation potentials (POCPs), global warming potentials (GWPs), ozone depletion potentials (ODPs) for haloolefins and related compounds.

Compound	Atmospheric lifetime	Radiative efficiency	POCP	GWP	ODP
Alkanes–alkenes					
CH_2=CH_2	1.4 d[a]	0.035	100[a,d]	<1	0
CH_3CH=CH_2	0.44 d[a]	0.035[b]	112.3[d]	<1	0
CH_3CH_2CH=CH_2	0.37 d[a]	0.035[b]	107.9[d]	<1	0
CH_4	12.4 years[c]	0.000363[e]	0.6	30[e]	0
C_2H_6	45 d[a]	0.0032[b]	12.3[d]	<1	0
C_3H_8	10 d[a]	0.0031[b]	17.6[d]	<1	0
n-C_4H_{10}	4.7 d[a]	0.0047[b]	35.2[d]	<1	0
CFCs					
CF_3Cl (CFC-11)	45 years[e]	0.26[e]	0.0	4660[e]	1.0[e]
CF_2Cl_2 (CFC-12)	100 years[e]	0.32[e]	0.0	10,200[e]	0.82[f]
HFCs					
CH_2F_2 (HFC-32)	5.2 years[g]	0.11[g]	0.2[h]	677[g]	0
CF_3CHF_2 (HFC-125)	28.2 years[g]	0.23[g]	0.0[h]	3170[g]	0
CF_3CH_3 (HFC-143a)	47.1 years[g]	0.16[g]	0.0[h]	4800[g]	0
CF_3CH_2F (HFC-134a)	13.4 years[g]	0.16[g]	0.1[h]	1300[g]	0
CHF_2CH_3 (HFC-152a)	1.5 years[g]	0.10[g]	1.0[h]	124[g]	0
CF_3CHFCF_3 (HFC-227ea)	38.9 years[g]	0.27[g]	0.0[i]	3350[g]	0
CF_3CH_2FCHF (HFC-245eb)	3.1 years[g]	0.20[g]	0.2[i]	290[g]	0
HFOs					
CF_2=CH_2 (HFO-1132a)	4.0 d[g]	0.00[g]	18.0[i]	<1[g]	0
CF_2=CF_2 (HFO-1114)	1.1 d[g]	0.00[g]	12.5[i]	<1[g]	0
CF_3CH=CH_2 (HFO-1243zf)	7.0 d[g]	0.01[g]	10.7[i]	<1[g]	0
CF_3CFH=CH_2 (HFO-1234yf)	10.5 d[g]	0.02[g]	7.0[i]	<1[g]	0
CF_3CF=CF_2 (HFO-1216)	4.9 d[g]	0.01[g]	5.4[i]	<1[g]	0
Z-CF_3CF=CHF (HFO-1225ye(Z))	8.5 d[g]	0.02[g]	5.6[i]	<1[g]	0
E-CF_3CF=CHF (HFO-1225ye(E))	4.9 d[g]	0.01[g]	7.3[i]	<1[g]	0
CF_3CF_2CH=CH_2 (HFO-1345zfc)	7.6 d[g]	0.01[g]	6.6[i]	<1[g]	0
t-CF_3CH=CHF (HFO-1234ze(E))	16.4 d[g]	0.04[g]	6.4[i]	<1[g]	0
Z-CF_3CH=$CHCF_3$ (HFO-1336(Z))	22.0 d[g]	0.07[g]	3.1[i]	2[g]	0
HCFOs					
E-CF_3CH=$CHCl$ (HCFO-1233zd(E))	26 d[g]	0.04[g]	3.9	1[g]	0.00034[k]
Z-CF_3CH=$CHCl$ (HCFO-1233zd(Z))	12 d[j]	0.02[j]	6.4[j]	<1[j]	<0.00034[k]

[a] Calvert et al. (2008).
[b] Highwood et al. (1999).
[c] By definition.
[d] Derwent et al. (1998).
[e] IPCC (2013).
[f] WMO (2011).
[g] Hodnebrog et al. (2013).
[h] Hayman and Derwent (1997).
[i] Wallington et al. (2010).
[j] Estimated using the method described by Jenkin (1998) with the following k(OH) data: Z-CF_3CH=$CHCF_3$ (HFO-1336(Z)), 4.91×10^{-13} (Baasandorj et al., 2011); E-$CHCl$=$CHCF_3$ (HCFO-1233zd(E)), 4.4×10^{-13} (Sulbaek Andersen et al., 2008); Z-$CHCl$=$CHCF_3$ (HCFO-1233zd(Z)), 9.4×10^{-13} (Andersen et al., 2014).
[k] Patten and Wuebbles (2010), see Section 5.
[l] Andersen et al. (2014).

As seen from Table 2, haloolefins have POCPs which are larger than those for analogous HFCs but much smaller than those for the parent alkenes. Haloolefins have POCPs which lie between those for methane (0.6) and ethane (12.3). Methane and ethane are oxidized sufficiently slowly that they do not contribute to any appreciable degree to local air quality issues and are generally exempt from air quality regulations (Dimitriades, 1999). Carter (2009) conducted Maximum Incremental Reactivity (MIR) calculations for CF_3CF=CHF and found that ozone production CF_3CF=CHF is indistinguishable from ethane (C_2H_6). Luecken et al. (2010) conducted an atmospheric modeling study and reported that replacing HFC-134a in vehicle air conditioning units with HFO-1234yf across the U.S. had essentially no impact (<0.01%) on tropospheric ozone formation. We conclude that the commercially relevant haloolefins will not make a significant contribution to tropospheric ozone formation.

We note that the POCP values for haloolefins given in Table 2 are *estimated* values. From the data presented by Derwent et al. (1998) and Jenkin (1998) we expect that estimated POCPs will not be materially different from those calculated in a more rigorous modeling approach. However, it would be useful to incorporate a detailed description of the atmospheric oxidation mechanisms of these haloolefins into a photochemical trajectory model and compare the results from such a rigorous analysis with the estimates provided here.

4. Global warming potentials (GWPs)

Haloolefins contain C—F bonds which absorb in the atmospheric window region and have the potential to contribute to radiative forcing of climate change (see Fig. 1). The radiative efficiency of a molecule reflects its heat trapping ability in the atmosphere, has units of $W\,m^{-2}\,ppb^{-1}$, and can be calculated using a radiative transfer model. As seen from Table 2, the estimated radiative efficiencies (REs) for the haloolefins are considerably smaller than the CFCs and HFCs they replace. The radiative efficiencies of haloolefins are low because of their non-uniform horizontal and vertical mix-

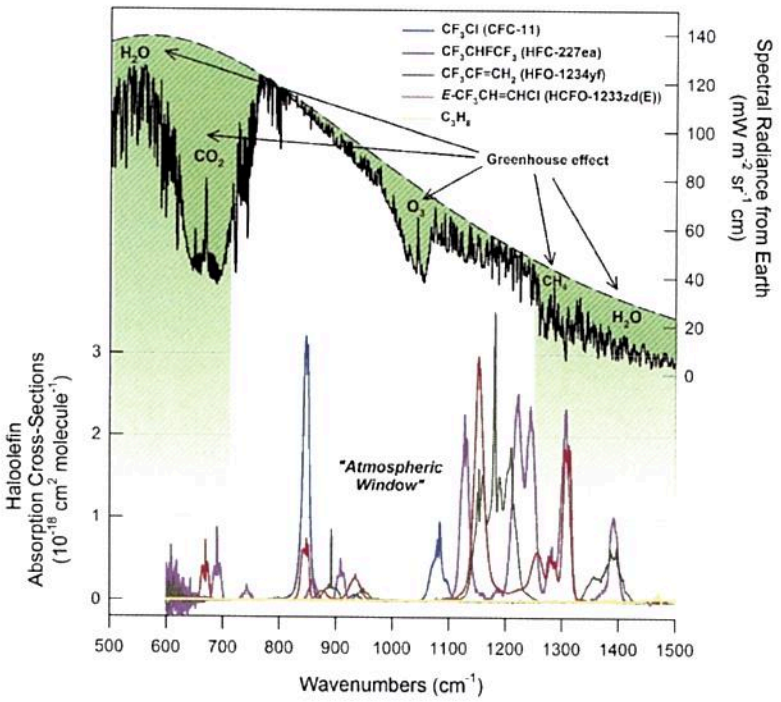

Fig. 1. The net upward atmospheric radiance spectrum at the tropopause (solid black trace), overlayed with the ideal Planck function for a blackbody emissions at 290 K (black dashed line). The presence of naturally occurring major greenhouse gases in the atmosphere (CO_2, H_2O, O_3 and CH_4) produces attenuation of the outgoing radiation resulting in a non-ideal Plank curve (i.e., the "natural greenhouse gas effect"). The IR spectra for CF_3Cl (blue trace), CF_3CHFCF_3 (pink trace), $CF_3CF=CH_2$ (green trace), E-$CF_3CH=CHCl$ (red trace), and the non-halogenated C_3H_8 (yellow trace) are shown (figure adapted from Sulbaek Andersen et al. (2012b)). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

ing in the atmosphere (Hodnebrog et al., 2013). Accounting for non-uniform horizontal mixing is important because radiative forcing is most efficient at lower latitudes where temperatures are higher. Accounting for non-uniform vertical mixing is important because radiative forcing is defined as the change in radiative flux at the tropopause which is located at approximately 12–15 km altitude (see Fig. 1). Mixing of haloolefins to lower latitudes and higher altitudes is inefficient and hence as seen in Table 2 the radiative efficiencies of haloolefins are small.

The global warming potential (GWP) is the integrated radiative forcing over a given time horizon following the pulsed emission of a kg of gas compared to the integrated radiative forcing for release of a kg of CO_2. As discussed above the radiative efficiencies of haloolefins are small and the atmospheric lifetimes of haloolefins are short. These two factors combine to give haloolefins very small GWPs as seen in Table 2. The atmospheric degradation products of haloolefins could in principle contribute to radiative forcing of climate change. However, it is well established that the oxidation products of haloolefins are removed from the atmosphere by wet and dry deposition on a time scale of days to weeks (Wallington et al., 1994). Haloolefins will not make any significant contribution to radiative forcing of climate change.

5. Ozone depletion potentials (ODPs)

In contrast to chlorine and bromine, fluorine does not participate in catalytic ozone destruction cycles (Ravishankara et al., 1994; Wallington et al., 1995). Hence, hydrofluoroolefins do not deplete stratospheric ozone and have an ozone depletion potential of zero. Chlorine and bromine containing haloolefins will contribute to stratospheric ozone depletion although the magnitude of such contribution is small because their short atmospheric lifetimes limit the fraction of the emissions which survive transport through the troposphere to the stratosphere. Patten and Wuebbles (2010) conducted a modeling study and derived an ODP for E-$CF_3CH=CHCl$ of 0.00034. The Z-isomer of $CF_3CH=CHCl$ has an atmospheric lifetime which is approximately half that of the E-isomer (Andersen et al., 2014) and hence the ODP for Z-$CF_3CH=CHCl$ will be even lower than that for E-$CF_3CH=CHCl$. Patten and Wuebbles (2010) concluded that at the concentrations likely to be emitted E-$CF_3CH=CHCl$ is unlikely to affect stratospheric ozone. Haloolefins have ODPs which are zero, or near zero, and will not impact stratospheric ozone.

6. Formation of noxious or toxic degradation products

Oxidation of haloolefins is initiated by addition of OH to the double bond giving a β-hydroxy alkyl radical which in one atmosphere of air will rapidly (within 10^{-6} s) add O_2 to give a β-hydroxy alkylperoxy radical. The peroxy radicals are converted by reaction with NO into alkoxy radicals which are converted into halogenated carbonyl compounds via either unimolecular decomposition, or reaction with O_2. As an example, Fig. 2 shows the oxidation mechanism for $CF_3CF=CH_2$. Halogenated carbonyl compounds are removed from the atmosphere via wet and dry deposition on a time scale of days to weeks (Wallington et al., 1994). Hydrolysis of halogenated carbonyl compounds gives acid and CO_2 products. Trifluoroacetic acid (CF_3COOH) is formed either though hydrolysis of carbonyl oxidation products or via secondary photochemistry. For example, the atmospheric fate of $CF_3C(O)F$, formed in the oxidation of $CF_3CF=CH_2$, is hydrolysis which occurs on a time scale of approximately 10 d to give $CF_3C(O)OH$ (Wallington et al., 1994). CF_3CHO, which is formed in the oxidation of $CF_3CH=CH_2$, undergoes photolysis (lifetime of $\leqslant$2 d) giving CF_3 and HCO radicals while reaction with OH, which is of lesser importance, but also represents a sink for CF_3CHO, gives CF_3CO radicals (Sulbaek

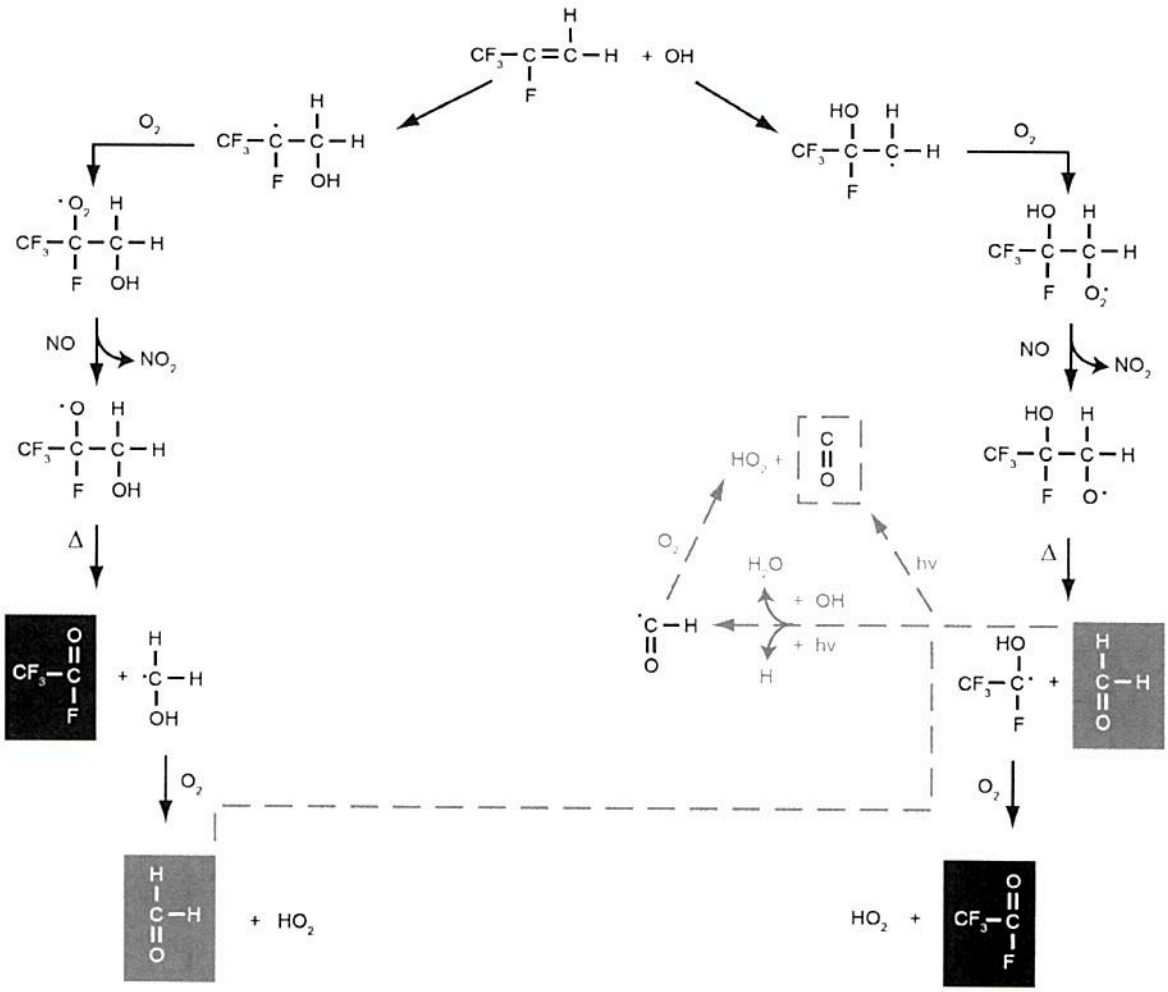

Fig. 2. Atmospheric degradation mechanism for $CF_3CF{=}CH_2$.

Andersen et al., 2004). Atmospheric degradation routes by which CF_3CO radicals can be transformed into CF_3COOH (TFA) as a minor product have been documented (Hurley et al. 2006).

In the case of HCFOs, chlorine substituted oxidation products are expected to be formed, including HCOCl. The atmospheric fate of the oxidation product HCOCl is incorporation into rain, cloud and fog water followed by hydrolysis and removal by wet deposition, within 5–15 d. Hydrolysis of HCOCl gives formic acid which is a ubiquitous component of the environment and is of no concern. For the HCFOs there is also evidence of a primary oxidation channel leading to chlorine atom elimination and formation of an enol, $CF_3CH{=}CHOH$ (Sulbaek Andersen et al., 2012a). The atmospheric fate of the enol is likely reaction with OH (directly, or indirectly via reaction with the tautomer form) to yield CF_3CHO, HCHO and HCOOH. The intermediate and final atmospheric degradation products of the commercially significant haloolefins are listed in Table 3.

Assuming that global emissions of haloolefins are of the order of 100 kt per year (i.e., similar to current hydrofluorocarbon emissions), an empirical formula of —CHX—(X = F or Cl) for these compounds, uniform distribution in the atmosphere, and annual global precipitation of 4.9×10^{17} L (Erchel, 1975) the level of HF/HCl expected from degradation of haloolefins would be of the order of 10^{-9}–10^{-8} molar. Haloolefins will not be uniformly distributed in the atmosphere and hence the regional concentrations of HF/HCl will be greater than the global average by perhaps an order of magnitude (i.e., 10^{-8}–10^{-7} molar). The concentration of fluoride/chloride and the additional acidity in precipitation resulting from the atmospheric oxidation of haloolefins will be negligible. Trifluoroacetic acid is a persistent degradation product of haloolefins containing the CF_3CF = group (e.g., $CF_3CF{=}CH_2$, $CF_3CF{=}CHF$). Its sources (natural and anthropogenic), sinks, and potential environmental effects have been reviewed by Tang et al. (1998), Solomon et al. (2003), and WMO (2007). It has been shown that trifluoroacetic acid is ubiquitous in precipitation and ocean water even in remote areas (Boutonnet et al., 1999; Berg et al., 2000;

Table 3
Atmospheric oxidation products of commercial haloolefins.

Haloolefin	Intermediate products	Final products
CF_3—$CF{=}CH_2$ (HFO-1234yf)	$CF_3C(O)F$, HCHO	$CF_3C(O)OH$, CO_2, HF
trans-CF_3—$CH{=}CHF$ (HFO-1234ze(E))	$CF_3C(O)H$, $HC(O)F$	CO_2, $HC(O)OH$, HF
CF_3—$CF{=}CF_2$ (HFO-1216)	$CF_3C(O)F$, COF_2	$CF_3C(O)OH$, CO_2, HF
E-CF_3—$CH{=}CHCl$ (1233zd(E))	$CF_3C(O)H$, $HC(O)Cl$, HCl, $CF_3CH{=}CHOH$	CO_2, HF, HCl
Z-CF_3—$CH{=}CHCl$ (1233zd(Z))	$CF_3C(O)H$, $HC(O)Cl$, HCl, $CF_3CH{=}CHOH$	CO_2, HF, HCl

Frank et al., 2002; Scott et al., 2005, 2006; Von Sydow et al. 2000). Frank et al. (2002) estimated that the oceans contain 268 million tonnes of trifluoroacetic acid. The natural environmental loading of trifluoroacetic acid greatly exceeds that expected from the atmospheric degradation of HFOs.

While Tromp et al. (1995) argued that trifluoroacetic acid will accumulate to high levels in seasonal wetlands, Boutonnet et al. (1999) showed that the assumptions made by Tromp et al. were highly improbable. Benesch et al. (2002) showed that trifluoroacetic acid does not adversely affect the development of soil microbial communities and pool plant species in vernal ponds. Modeling studies by Luecken et al. (2010) and Russell et al. (2012) have concluded that levels of trifluoroacetic acid resulting from extended (50 years) use of HFO-1234yf would not represent a risk to ecosystems in the U.S. With respect to trifluoroacetic acid formation from the atmospheric degradation of hydrofluorochlorocarbons (HCFCs) and hydrofluorocarbons (HFCs) it has been concluded that "trifluoroacetic acid from the degradation of HCFCs and HFCs will not result in environmental concentrations capable of significant ecosystem damage" (WMO, 2007). The same conclusion is applicable for short-chain haloolefins.

7. Discussion

There is an extensive body of data concerning the atmospheric chemistry of haloolefins and the atmospheric oxidation mechanism for these compounds is well understood. Haloolefins react rapidly with OH radicals and as a result have short atmospheric lifetimes and negligible GWPs. The ability of haloolefins to contribute to tropospheric ozone formation is negligible, the oxidation products of short-chain haloolefins are benign. The commercially relevant short-chain haloolefins $CF_3CF{=}CH_2$ (1234yf), *trans*-$CF_3CH{=}CHF$ (1234ze(Z)), $CF_3CF{=}CF_2$ (1216), *cis*-$CF_3CH{=}CHCl$ (1233zd(Z)), and *trans*-$CF_3CH{=}CHCl$ (1233zd(E)) can be considered to be environmentally acceptable.

Acknowledgements

O.J.N. acknowledges financial support from the Danish Natural Science Research Council and the Villum Kann Rasmussen Foundation for the Copenhagen Center for Atmospheric Research (CCAR).

References

Andersen, L., Sulbaek Andersen, M.P., Wallington, T.J., Nielsen, O.J., 2014. Unpublished Data.

Baasandorj, M., Ravishankara, A.R., Burkholder, J.B., 2011. Atmospheric chemistry of (Z)-$CF_3CH{=}CHCF_3$: OH radical reaction rate coefficient and global warming potential. J. Phys. Chem. A 115, 10539–10549.

Berg, M., Muller, S.R., Mühlemann, J., Wiedmer, A., Scharzenbach, R.P., 2000. Concentrations and fluxes of chloroacetic acids and trifluoroacetic acid in rain and natural waters in Switzerland. Environ. Sci. Technol. 34, 2675–2683.

Benesch, J.A., Gustin, M.S., Cramer, G.R., Cahill, T.M., 2002. Investigation of effects of trifluoroacetate on vernal pool ecosystems. Environ. Toxicol. Chem. 21, 640–647.

Bintein, S., Devillers, J., Karcher, W., 1993. Nonlinear dependence of fish bioconcentration on n-octanol/water partition coefficients. SAR QSAR Environ. Res. 1, 29–39.

Brown, J.S., 2009. HFOs new, low global warming potential refrigerants. ASHRAE J. 51, 22–29.

Boutonnet, J.C., Bingham, P., Calamari, D., de Rooij, C., Franklin, J., Kawano, T., Libre, J.-M., McCulloch, A., Malinverno, G., Odom, J.M., Rusch, G.M., Smythe, K., Sobolev, I., Thompson, R., Tiedje, J.M., 1999. Environmental risk assessment of trifluoroacetic acid. Hum. Ecol. Risk Assess. 5, 59–124.

Carter, W.P.L., 2009. Investigation of atmospheric ozone impacts of trans 2,3,3,3-tetrafluoropropene. Final Report for Contract UCR-09010016. <http://www.cert.ucr.edu/~carter/pubs/YFrept.pdf>.

Calvert, J.G., Derwent, R.G., Orlando, J.J., Tyndall, G.S., Wallington, T.J., 2008. Mechanisms of Atmospheric Oxidation of the Alkanes. Oxford University Press, Oxford, UK. ISBN 978-0-19-536581-8.

Calvert, J.G., Mellouki, A., Orlando, J.J., Pilling, M.J., Wallington, T.J., 2011. Mechanisms of Atmospheric Oxidation of the Oxygenates. Oxford University Press, Oxford, UK.

Derwent, R.G., Jenkin, M.E., Saunders, S.M., 1996. Photochemical ozone creation potentials for a large number of reactive hydrocarbons under European conditions. Atmos. Environ. 30, 181–199.

Derwent, R.G., Jenkin, M.E., Saunders, S.M., Pilling, M.J., 1998. Photochemical ozone creation potentials for organic compounds in North West Europe calculated with a master chemical mechanism. Atmos. Environ. 32, 2429–2441.

Dimitriades, B., 1999. Scientific basis of an improved EPA policy on control of organic emissions for ambient ozone reduction. J. Air Waste Manage. Assoc. 49, 831–838.

Erchel, E., 1975. World Water Balance. Elsevier.

Farman, J.D., Gardiner, B.G., Shanklin, J.D., 1985. Large losses of total ozone in Antarctica reveal seasonal ClO_x/NO_x interaction. Nature 315, 207–210.

Frank, H., Christoph, E.H., Holm-Hansen, O., Bullister, J.L., 2002. Trifluoroacetate in ocean waters. Environ. Sci. Technol. 36, 12–15.

Hayman, G.D., Derwent, R.G., 1997. Atmospheric chemical reactivity and ozone forming potentials of potential CFC replacements. Environ. Sci. Technol. 31, 327–336.

Highwood, E.J., Shine, K.P., Hurley, M.D., Wallington, T.J., 1999. Estimation of direct radiative forcing due to non-methane hydrocarbons. Atmos. Environ. 33, 759–767.

Hodnebrog, Ø., Etminan, M., Fuglesvedt, J.S., Marston, G., Myhre, G., Nielsen, C.J., Shine, K.P., Wallington, T.J., 2013. Global warming potentials and radiative efficiencies of halocarbons and related compounds: a comprehensive review. Rev. Geophys. 51, 300–378.

Hurley, M.D., Ball, J.C., Wallington, T.J., Sulbaek Andersen, M.P., Nielsen, O.J., Ellis, D.A., Martin, J.W., Mabury, S.A., 2006. Atmospheric Chemistry of n-$C_xF_{2x+1}CHO$ (x = 1, 2, 3, 4):Fate of n-$C_xF_{2x+1}C(O)$ Radicals. J. Phys. Chem. A 110, 12443–12447.

IPCC (Intergovernmental Panel on Climate Change), 2013. Climate change 2013: The physical science basis. Cambridge University Press, Cambridge, UK.

Jenkin, M.E., 1998. Photochemical Ozone and PAN Creation Potentials: Rationalisation and Methods of Estimation. AEA Technology plc, Report AEAT-4182/20150/003, AEA Technology plc. National Environmental Technology Centre, Culham, Oxfordshire OX14 3DB, UK.

Luecken, D.J., Waterland, R.L., Papasavva, S., Taddonio, K., Hutzell, W.T., Rugh, J.P., Andersen, S.O., 2010. Ozone and TFA impacts in North America from degradation of 2,3,3,3-tetrafluoropropene (HFO-1234yf), a potential greenhouse gas replacement. Environ. Sci. Technol. 44, 343–348.

Molina, M.J., Rowland, F.S., 1974. Stratospheric sink for chlorofluoromethanes: chlorine atom-catalysed destruction of ozone. Nature 249, 810–812.

Patten, K.O., Wuebbles, D.J., 2010. Atmospheric lifetimes and ozone depletion potentials of trans-1-chloro-3,3,3-trifluoropropylene and trans-1,2-dichloroethylene in a three-dimensional model. Atmos. Chem. Phys. 10, 10867–10874.

Ravishankara, A.R., Turnipseed, A.A., Jensen, N.R., Barone, S., Mills, M., Howard, C.J., Solomon, S., 1994. Do hydrofluorocarbons destroy stratospheric ozone. Science 263, 71–75.

Russell, M.H., Hoogeweg, G., Webster, E.M., Ellis, D.A., Waterland, R.L., Hoke, R.A., 2012. TFA from HFO-1234yf: Accumulation and aquatic risk in terminal water bodies. Environ. Toxicol. Chem. 31, 1957–1965.

Scott, B.F., Macdonald, R.W., Kannan, K., Fisk, A., Witter, A., Yamashita, N., Durham, L., Spencer, C., Muir, D.C.G., 2005. Trifluoroacetate profiles in the Arctic, Atlantic, and Pacific Oceans. Environ. Sci. Technol. 39, 6555–6560.

Scott, B.F., Spencer, C., Mabury, S.A., Muir, D.C.G., 2006. Poly and perfluorinated carboxylates in North American precipitation. Environ. Sci. Technol. 40, 7167–7174.

Singh, R., 2014. Honeywell International Inc., Private Communication.

Solomon, K.R., Tang, X., Wilson, S.R., Zanis, P., Bais, A.F., 2003. Changes in tropospheric composition and air quality due to stratospheric ozone depletion. Photochem. Photobiol. Sci. 2, 62–67.

Sulbaek Andersen, M.P., Nielsen, O.J., Hurley, M.D., Ball, J.C., Wallington, T.J., Stevens, J.E., Martin, J.W., Ellis, D.A., Mabury, S.A., 2004. Atmospheric chemistry of n-$C_xF_{2x+1}CHO$ (x = 1, 3, 4): reaction with Cl atoms, OH radicals and IR spectra of $C_xF_{2x+1}C(O)O_2NO_2$. J. Phys. Chem. A 108, 5189–5196.

Sulbaek Andersen, M.P., Nilsson, E.J.K., Nielsen, O.J., Johnson, M.S., Hurley, M.D., Wallington, T.J., Singh, R., 2008. Atmospheric Chemistry of trans-$CF_3CH{=}CHCl$: Kinetics of the gas-phase reactions with Cl atoms, OH radicals, and O_3. J. Photochem. Photobiol. A: Chem. 199, 92–97.

Sulbaek Andersen, M.P., Nielsen, O.J., Hurley, M.J., Wallington, T.J., 2012a. Atmospheric chemistry of t-$CF_3CH{=}CHCl$: products and mechanisms of the gas-phase reactions with chlorine atoms and hydroxyl radicals. Phys. Chem. Chem. Phys. 14, 1735–1748.

Sulbaek Andersen, M.P., Nielsen, O.J., Wallington, T.J., 2012b. Assessing the impact on global climate from general anesthetic gases. Anesth. Analg. 114, 1081–1084.

Tang, X., Madronich, S., Wallington, T., Calamari, D., 1998. Changes in tropospheric composition and air quality. J. Photoch. Photobio, B 46, 83–95.

Tromp, T.K., Ko, M.K.W., Rodriguez, J.M., Sze, N.D., 1995. Potential accumulation of a CFC-replacement degradation product in seasonal wetlands. Nature 376, 327–330.

Von Sydow, L.M., Grimvall, A.B., Borén, H.B., Laniewski, K., Nielsen, A.T., 2000. Natural background levels of trifluoroacetate in rain and snow. Environ. Sci. Technol. 34, 3115–3118.

Wallington, T.J., Schneider, W.F., Sehested, J., Nielsen, O.J., 1995. Hydrofluorocarbons and stratospheric ozone. Faraday Discuss. 100, 55–64.

Wallington, T.J., Schneider, W.F., Worsnop, D.R., Nielsen, O.J., Sehested, J., Debruyn, W.J., Shorter, J.A., 1994. The environmental-impact of CFC replacements – HFCs and HCFCs. Environ. Sci. Technol. 28, A320–A326.

Wallington, T.J., Sulbaek Andersen, M.P., Nielsen, O.J., 2010. Estimated photochemical ozone creation potentials (POCPs) of $CF_3CF{=}CH_2$ (HFO-1234yf) and related hydrofluoroolefins (HFOs). Atmos. Environ. 44, 1478–1481.

WMO (World Meteorological Organization), 2007. Scientific Assessment of Ozone Depletion: 2006, Global Ozone, Research and Monitoring Project – Report 50, Geneva, Switzerland.

WMO (World Meteorological Organization), 2011. Scientific Assessment of Ozone Depletion: 2010, Global Ozone, Research and Monitoring Project – Report 52, Geneva, Switzerland.

SAFETY DATA SHEET

Honeywell

cis-1-Chloro-3,3,3-Trifluoropropene (synonyms 1-Chloro-3,3,3-trifluoropropene(Z), cis-1233zd and 1233zd(Z))

000000017624

Version 1.2 | Revision Date 01/05/2017 | Print Date 01/05/2017

SECTION 1. PRODUCT AND COMPANY IDENTIFICATION

Product name	:	cis-1-Chloro-3,3,3-Trifluoropropene (synonyms 1-Chloro-3,3,3-trifluoropropene(Z), cis-1233zd and 1233zd(Z))
Number	:	000000017624
Product Use Description	:	Solvent
Note	:	This sample is for research and development purposes only. The handling and use of this material must be supervised by qualified individuals. The chemical, physical and toxicological properties of this material have not been fully investigated. Use due precaution in handling, storage and disposal.
Manufacturer or supplier's details	:	Honeywell International Inc. 115 Tabor Road Morris Plains, NJ 07950-2546
For more information call	:	800-522-8001 +1-973-455-6300 (Monday-Friday, 9:00am-5:00pm)
In case of emergency call	:	**Medical: 1-800-498-5701 or +1-303-389-1414** **Transportation (CHEMTREC): 1-800-424-9300 or +1-703-527-3887** : (24 hours/day, 7 days/week)

SECTION 2. HAZARDS IDENTIFICATION

Emergency Overview

Form	:	liquid, clear
Color	:	colourless
Odor	:	slight

Classification of the substance or mixture

Not a dangerous substance or mixture according to the Globally Harmonised System (GHS).

Precautionary statements : **Prevention:**
Use personal protective equipment as required.

Hazards not otherwise classified : Excessive exposure may cause central nervous system effects including drowsiness and dizziness. Excessive exposure may also cause cardiac arrhythmia.

Carcinogenicity

No component of this product present at levels greater than or equal to 0.1% is identified as a known or anticipated carcinogen by NTP, IARC, or OSHA.

SECTION 3. COMPOSITION/INFORMATION ON INGREDIENTS

Synonyms : 1-Chloro-3,3,3-trifluoropropene(Z), cis-1233zd and 1233zd(Z)

Formula : C3H2ClF3

Chemical nature : Substance

Chemical name	CAS-No.	Concentration
cis-1-Chloro-3,3,3-trifluoropropene (1233zd(Z))	99728-16-2	>99.00 %

SECTION 4. FIRST AID MEASURES

Inhalation : Remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Use oxygen as required, provided a qualified operator is present. Call a physician.

Skin contact : After contact with skin, wash immediately with plenty of water. If symptoms persist, call a physician. Take off all contaminated clothing immediately. Wash contaminated clothing before re-use.

Eye contact : Rinse immediately with plenty of water, also under the eyelids, for at least 15 minutes. Call a physician if irritation develops or

persists.

Ingestion : Do not induce vomiting without medical advice. Never give anything by mouth to an unconscious person. Call a physician immediately.

Notes to physician

Treatment : Treat symptomatically.

SECTION 5. FIREFIGHTING MEASURES

Suitable extinguishing media : The product is not flammable.
Use extinguishing measures that are appropriate to local circumstances and the surrounding environment.
Water spray
Carbon dioxide (CO2)
Dry chemical
Foam

Specific hazards during firefighting : This product is not flammable at ambient temperatures and atmospheric pressure.
However, this material can ignite when mixed with air under pressure and exposed to strong ignition sources.
Container may rupture on heating.
Cool closed containers exposed to fire with water spray.
Do not allow run-off from fire fighting to enter drains or water courses.
Vapours are heavier than air and can cause suffocation by reducing oxygen available for breathing.
Exposure to decomposition products may be a hazard to health.
In case of fire hazardous decomposition products may be produced such as:
Hydrogen fluoride
Gaseous hydrogen chloride (HCl).
Carbon monoxide
Carbon dioxide (CO2)
Carbonyl halides

Special protective equipment for firefighters : In the event of fire and/or explosion do not breathe fumes.
Wear self-contained breathing apparatus and protective suit.
No unprotected exposed skin areas.

SECTION 6. ACCIDENTAL RELEASE MEASURES

Personal precautions	:	Immediately evacuate personnel to safe areas. Keep people away from and upwind of spill/leak. Wear personal protective equipment. Unprotected persons must be kept away. Remove all sources of ignition. Ventilate the area. Vapours are heavier than air and can cause suffocation by reducing oxygen available for breathing. Avoid accumulation of vapours in low areas. Unprotected personnel should not return until air has been tested and determined safe. Ensure that the oxygen content is >= 19.5%.
Environmental precautions	:	Should not be released into the environment. Do not flush into surface water or sanitary sewer system. Prevent further leakage or spillage if safe to do so. Prevent spreading over a wide area (e.g. by containment or oil barriers).
Methods for cleaning up	:	Contain spillage, and then collect with non-combustible absorbent material, (e.g. sand, earth, diatomaceous earth, vermiculite) and place in container for disposal according to local / national regulations (see section 13).

SECTION 7. HANDLING AND STORAGE

Handling

Handling	:	Handle with care. Do not use in areas without adequate ventilation. Perform filling operations only at stations with exhaust ventilation facilities. Open drum carefully as content may be under pressure. Wash thoroughly after handling. Do not eat, drink or smoke when using this product. Do not swallow. Do not breathe vapours or spray mist. Avoid contact with skin, eyes and clothing.

Advice on protection against fire and explosion	:	Can form a combustible mixture with air at pressures above atmospheric pressure. Keep product and empty container away from heat and sources of ignition.

Storage

Requirements for storage areas and containers	:	Keep containers tightly closed in a dry, cool and well-ventilated place. Storage rooms must be properly ventilated. Store in original container. Keep away from direct sunlight. Protect from physical damage. Store away from incompatible substances.

SECTION 8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Protective measures	:	Ensure that eyewash stations and safety showers are close to the workstation location. Do not breathe vapours or spray mist. Avoid contact with skin, eyes and clothing.
Engineering measures	:	Use with local exhaust ventilation. Perform filling operations only at stations with exhaust ventilation facilities.
Eye protection	:	Do not wear contact lenses. Wear as appropriate: Goggles or face shield, giving complete protection to eyes
Hand protection	:	Impervious gloves Gloves must be inspected prior to use. Replace when worn.
Skin and body protection	:	Wear as appropriate: Solvent-resistant gloves Solvent-resistant apron and boots If splashes are likely to occur, wear: Protective suit
Respiratory protection	:	In case of insufficient ventilation wear suitable respiratory equipment.

For rescue and maintenance work in storage tanks use self-contained breathing apparatus.
Use NIOSH approved respiratory protection.

Hygiene measures : Handle in accordance with good industrial hygiene and safety practice.
Avoid contact with skin, eyes and clothing.
Do not breathe vapours or spray mist.
Ensure adequate ventilation, especially in confined areas.
Remove and wash contaminated clothing before re-use.
Contaminated work clothing should not be allowed out of the workplace.
Keep working clothes separately.
Wash hands before breaks and immediately after handling the product.

Exposure Guidelines
Contains no substances with occupational exposure limit values.

SECTION 9. PHYSICAL AND CHEMICAL PROPERTIES

Physical state	:	liquid, clear
Color	:	colourless
Odor	:	slight
Melting point/range	:	Note: not determined
Boiling point/boiling range	:	39 °C
Flash point	:	Note: Not applicable
Lower explosion limit	:	Note: None
Upper explosion limit	:	Note: None
Vapor pressure	:	595 hPa

		at 25 °C(77 °F)
Vapor density	:	Note: (Air = 1.0), not determined
Density	:	1.3 g/cm3 at 25 °C
Water solubility	:	Note: not determined
Ignition temperature	:	Note: not determined
Molecular weight	:	130.5 g/mol

SECTION 10. STABILITY AND REACTIVITY

Possibility of hazardous reactions	:	Polymerization can occur.
Conditions to avoid	:	Protect from heat/overheating. Keep away from direct sunlight. Heat, flames and sparks. Do not mix with oxygen or air above atmospheric pressure.
Incompatible materials to avoid	:	Strong oxidizing agents Magnesium Aluminium
Hazardous decomposition products	:	In case of fire hazardous decomposition products may be produced such as: Carbon monoxide Carbon dioxide (CO2) Carbonyl halides Gaseous hydrogen chloride (HCl). Gaseous hydrogen fluoride (HF).

SECTION 11. TOXICOLOGICAL INFORMATION

Acute inhalation toxicity	:	LC50: 36021 - 53352 ppm, vapour Exposure time: 4 h Species: Rat, male and female
	:	No-observed-effect level: 2500 ppm Species: dogs Symptoms: Cardiac sensitization
	:	Threshold limits: 5000 ppm Species: dogs Symptoms: Cardiac sensitization
Repeated dose toxicity	:	Species: Rat, male and female Application Route: Oral Exposure time: 28 d No observed adverse effect level: 300 mg/kg/d
	:	Species: Rat, male and female Application Route: inhalation (vapour) Exposure time: 13 Weeks No observed adverse effect level: 5000 ppm
Genotoxicity in vitro	:	Test Method: Mutagenicity (Salmonella typhimurium - reverse mutation assay) Metabolic activation: with and without metabolic activation Result: negative
	:	Test Method: Chromosome aberration test in vitro Cell type: Human lymphocytes Metabolic activation: with and without metabolic activation Result: negative
Genotoxicity in vivo	:	Test Method: unscheduled DNA synthesis assay Species: Rat Application Route: inhalation (vapour) Result: negative
Genotoxicity in vivo	:	Test Method: Micronucleus test Species: Rat Application Route: inhalation (vapour)

Result: negative

SECTION 12. ECOLOGICAL INFORMATION

Ecotoxicity effects

Toxicity to fish	:	semi-static test LC50: 46.8 mg/l Exposure time: 96 h Species: Oncorhynchus mykiss (rainbow trout) Method: OECD Test Guideline 203
Toxicity to daphnia and other aquatic invertebrates	:	static test EC50: 27.6 mg/l Exposure time: 48 h Species: Daphnia magna (Water flea) Method: OECD Test Guideline 202
Toxicity to algae	:	Growth inhibition EC50: > 97.5 mg/l Exposure time: 72 h Species: Pseudokirchneriella subcapitata (green algae)
	:	Growth rate EC50: > 97.5 mg/l Exposure time: 72 h Species: Pseudokirchneriella subcapitata (green algae)
	:	Biomass EC50: > 97.5 mg/l Exposure time: 72 h Species: Pseudokirchneriella subcapitata (green algae)
	:	NOEC: 41 mg/l Exposure time: 72 h Species: Pseudokirchneriella subcapitata (green algae)

Further information on ecology

SECTION 13. DISPOSAL CONSIDERATIONS

Disposal methods	:	Observe all Federal, State, and Local Environmental regulations.
Note	:	Where possible recycling is preferred to disposal or incineration.

SECTION 14. TRANSPORT INFORMATION

DOT	Not dangerous goods
TDG	Not dangerous goods
IATA	Not dangerous goods
IMDG	Not dangerous goods

SECTION 15. REGULATORY INFORMATION

Inventories

US. Toxic Substances Control Act	:	Not On TSCA Inventory
Australia. Industrial Chemical (Notification and Assessment) Act	:	Not in compliance with the inventory
Canada. Canadian Environmental Protection Act (CEPA). Domestic Substances List (DSL)	:	Not in compliance with the inventory
Japan. Kashin-Hou Law List	:	Not in compliance with the inventory
Korea. Toxic Chemical Control Law (TCCL) List	:	Not in compliance with the inventory
Philippines. The Toxic Substances and Hazardous and Nuclear Waste Control	:	Not in compliance with the inventory

Act

China. Inventory of Existing Chemical Substances	:	Not in compliance with the inventory
New Zealand. Inventory of Chemicals (NZIoC), as published by ERMA New Zealand	:	Not in compliance with the inventory

National regulatory information

TSCA	:	This material must be used in compliance with the TSCA Research and Development Exemption requirements (40 CFR 720.36).
SARA 302 Components	:	No chemicals in this material are subject to the reporting requirements of SARA Title III, Section 302.
SARA 313 Components	:	This material does not contain any chemical components with known CAS numbers that exceed the threshold (De Minimis) reporting levels established by SARA Title III, Section 313.
SARA 311/312 Hazards	:	Acute Health Hazard
California Prop. 65	:	This product does not contain any chemicals known to State of California to cause cancer, birth defects, or any other reproductive harm.

SECTION 16. OTHER INFORMATION

		HMIS III	NFPA
Health hazard	:	1	2

Flammability	: 0	0
Physical Hazard	: 0	
Instability	:	0

Hazard rating and rating systems (e.g. HMIS® III, NFPA): This information is intended solely for the use of individuals trained in the particular system.

Further information

The information provided in this Safety Data Sheet is correct to the best of our knowledge, information and belief at the date of its publication. The information given is designed only as a guidance for safe handling, use, processing, storage, transportation, disposal and release and is not to be considered a warranty or quality specification. The information relates only to the specific material designated and may not be valid for such material used in combination with any other materials or in any process, unless specified in the text. Final determination of suitability of any material is the sole responsibility of the user. This information should not constitute a guarantee for any specific product properties.

Changes since the last version are highlighted in the margin. This version replaces all previous versions.
Previous Issue Date: 04/30/2013
Prepared by Honeywell Performance Materials and Technologies Product Stewardship Group

PRESS FIRMLY TO SEAL

US POSTAGE $023.75

ZIP 07950
041L11257894

PRIORITY ★ MAIL ★ EXPRESS™

OUR FASTEST SERVICE IN THE U.S.

WHEN USED INTERNATIONALLY, A CUSTOMS DECLARATION LABEL MAY BE REQUIRED.

EMS

EP13F July 2013 OD: 12.5 x 9.5

PS10001000006

1A

1B

WRITE FIRMLY WITH BALL POINT PEN ON HARD SURFACE TO MAKE ALL COPIES LEGIBLE.

CUSTOMER USE ONLY

FROM: (PLEASE PRINT) PHONE (973) 455-3102

Nicole Sandomenico
Honeywell
115 Tabor Road
Morris Plains, NJ 07950

PAYMENT BY ACCOUNT (if applicable)

USPS® Corporate Acct. No.	Federal Agency Acct. No. or Postal Service™ Acct. No.

DELIVERY OPTIONS (Customer Use Only)

☐ **SIGNATURE REQUIRED** Note: The mailer must check the "Signature Required" box if the mailer: 1) Requires the addressee's signature; OR 2) Purchases additional insurance; OR 3) Purchases COD service; OR 4) Purchases Return Receipt service. If the box is not checked, the Postal Service will leave the item in the addressee's mail receptacle or other secure location without attempting to obtain the addressee's signature on delivery.

Delivery Options

☐ No Saturday Delivery (delivered next business day)
☐ Sunday/Holiday Delivery Required (additional fee, where available*)
☐ 10:30 AM Delivery Required (additional fee, where available*)
*Refer to USPS.com® or local Post Office™ for availability.

TO: (PLEASE PRINT) PHONE (919) 541-4359

Dr Souad Benromdhane
Risks + Benefits Group
HEID, OAQPS, Mail Drop: C539-07
Research Triangle Park, NC

ZIP + 4® (U.S. ADDRESSES ONLY)

2 7 7 1 1 - _ _ _ _

- For pickup or USPS Tracking™, visit USPS.com or call 800-222-1811.
- $100.00 insurance included.

EL 303154208 US

UNITED STATES POSTAL SERVICE® | PRIORITY ★ MAIL ★ EXPRESS™

ORIGIN (POSTAL SERVICE USE ONLY)

☐ 1-Day ☐ 2-Day ☐ Military ☐ DPO

PO ZIP Code	Scheduled Delivery Date (MM/DD/YY)	Postage	
		$	
Date Accepted (MM/DD/YY)	Scheduled Delivery Time ☐ 10:30 AM ☐ 3:00 PM ☐ 12 NOON	Insurance Fee $	COD Fee $
Time Accepted ☐ AM ☐ PM	10:30 AM Delivery Fee $	Return Receipt Fee $	Live Animal Transportation Fee $
Weight ☐ Flat Rate lbs. ozs	Sunday/Holiday Premium Fee $	Total Postage & Fees $	
	Acceptance Employee Initials		

DELIVERY (POSTAL SERVICE USE ONLY)

Delivery Attempt (MM/DD/YY)	Time ☐ AM ☐ PM	Employee Signature
Delivery Attempt (MM/DD/YY)	Time ☐ AM ☐ PM	Employee Signature

LABEL 11-B, SEPTEMBER 2015 PSN 7690-02-000-9996 1-ORIGIN POST OFFICE COPY

VISIT US AT USPS.COM®

UNITED STATES POSTAL SERVICE